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ON THE ACTION OF AMMONIA ON ACETONEDICARBONIC ETHYL ESTER. SYNTHESIS OF PYRIDINE DERIVATIVES.[1]

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Acetonedicarbonic acid[2] and ammonia react violently; the products have not been isolated. Alcoholic ammonia appears to be almost without action on *acetonedicarbonic ethyl ester* in the cold; on heating, carbon dioxide is split off, forming ammonium carbamate and other not examined products.

The action of aqueous ammonia on the ether is much smoother, two bodies being formed, according to the conditions observed. If the ester is mixed with ordinary aqueous ammonia, and cooled with ice, a deposit of colorless needles is formed. When removed from the mother liquor this body fuses at a low temperature (under 15°), and cannot again be got to solidify. Apparently the same substance is formed by passing ammonia gas into the ester, pure or diluted with ordinary ether. The substance is quite readily soluble in ether and alcohol, and is decomposed instantly by acids into ammonia and acetonedicarbonic ethyl ester. It was not analysed, but is probably the analogue of the ammonia derivative of acetacetic ester,[3] when crystallised perhaps $C(OH)(NH_2)(CH_2.CO_2C_2H_5)_2$, and when liquid $C(NH)(CH_2.CO_2C_2H_5)_2$.

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[1] Preliminary Notice, Berichte **18**, 2290.

[2] Von Pechmann, Berichte **17**, 2542.

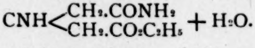
[3] Collie, Liebig's Annalen **226**, 298.

A much more stable body is formed by longer action of very concentrated aqueous ammonia on the ester. The ester used must be nearly pure, such as that obtained by saturating a mixture of equal parts acetonedicarbonic acid and alcohol with hydrochloric acid gas, diluting, and extracting the ester with ether. That obtained by adding alcohol to the direct product of the action of sulphuric on citric acid[1] has proved absolutely useless for this purpose.

To 1 volume acetonedicarbonic ester contained in a wide-mouthed bottle and cooled in ice and salt is added carefully, to prevent mixing, 1 volume of aqueous ammonia saturated in a freezing mixture. The bottle is then tightly closed and the contents mixed. If the mixture separates into two layers, more ammonia must be passed in, with cooling, until perfect solution is obtained. Crystals of the above-mentioned easily fusible compound are deposited, but some disappear. After standing two days at ordinary temperature the contents of the bottle become converted into a firm mass of greenish crystals, which are sucked out in a funnel with the pump and dried on porous plates. More may be obtained by allowing the strongly ammoniacal filtrate to stand in the open air in shallow vessels. The brown mass is washed with ether and recrystallised from water, avoiding too long heating. The snow-white product is freed from the dark fluorescent mother liquor by washing in a funnel with a little cold water. Thus obtained it is nearly pure, but becomes brownish by long keeping. After two or three recrystallisations from water it is perfectly pure, and may be kept without change indefinitely. The yield is about 70 per cent. of the theoretical.

	Calculated for $C_7H_{14}N_2O_4$.	Found.	
C	44.21	44.10	44.24
H	7.37	7.32	7.35
N	14.74	14.52	14.41

The properties of the body agree with the formula



$$CNH<\begin{matrix}CH_2.CONH_2\\CH_2.CO_2C_2H_5\end{matrix} + H_2O.$$

Whether the water is crystal water could not be decided. On gently heating, water and ammonia are given off simultaneously. It may be designated *β-imidoglutamic ethyl ester.*[2]

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[1] Berichte **18**, 468 Ref.

[2] The name β-oxyamidoglutamic ethyl ester, first adopted, Berichte **18**, 2291, is rejected, as no proof of the existence of hydroxyl in the body has been obtained.

The body forms long, flat, colorless, flexible needles. It fuses at 86°, and if heated higher, gives off water and ammonia. It is difficultly soluble in cold, readily in hot water and in alcohol, moderately in hot chloroform and difficultly in ether. Ferric chloride colors its solution deep red. Its aqueous solution soon decomposes, giving off ammonia and becoming yellow, and leaving on evaporation a greenish substance insoluble in alcohol. Cold dilute acids dissolve it, splitting off ammonia. Platinum chloride at once produces ammonium chloroplatinate. From its solution in dilute hydrochloric acid ether extracts a small quantity of a body fusing at 61°, and giving a purple color with ferric chloride. Sodium nitrite, added in excess to its acid solution, produces a precipitate, which, recrystallised from water or alcohol, forms small yellow needles, fusing at 178°, with evolution of hydrocyanic acid, etc. It appears to be an isonitroso-compound, but the few analyses made did not agree with any probable formula. It dissolves in alkali, but not in dilute acids, and gives no reaction with phenol and sulphuric acid.

Glutazine[1] *or Dioxyamidopyridine.*

β-Imidoglutamic ethyl ester is insoluble in cold solutions of alkalis or alkaline carbonates. By boiling with a carbonate it is decomposed, partly according to the reaction

$$C_7H_{14}N_2O_4 = C_5H_6N_2O_2 + C_2H_6O + H_2O.$$

One part substance is boiled with one part crystallised soda and 3—4 parts water for about ten minutes, or until a sample on cooling gives no crystals on rubbing the inside of the tube with a glass rod. On acidifying the cooled liquid with acetic acid a nearly colorless crystalline powder is thrown down, which is washed with cold water and alcohol. Thus prepared it is practically pure, but may be once recrystallised from water. The yield is about 40 per cent. of the theoretical. The remainder of the ester appears to undergo deeper decomposition, ammonia being given off and products formed which could not be isolated.

	Calculated for $C_5H_6N_2O_2$.	Found.	
C	47.62	47.62	47.34
H	4.76	4.84	4.77
N	22.22	22.68	22.33

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[1] Berichte **18**, 2291.

αα'-Dioxy-γ-amidopyridine forms colorless rectangular plates, or bunches of pointed crystals with serrated edges, sometimes also comb-like aggregates resembling sal ammoniac. When precipitated from its alkaline solution it forms a heavy, sandy powder. Frequently it has a greenish or yellowish tint, which cannot be removed by recrystallising. It fuses above 300°, with total decomposition and evolution of ammonia, leaving a very difficultly combustible coal. It is difficultly soluble in cold, moderately in hot water, nearly insoluble in hot alcohol, and insoluble in all other neutral solvents and acetic acid. Its reaction is acid. No ammonia is evolved on boiling with concentrated alkalis. It has acid properties, decomposing soluble or insoluble carbonates on boiling, forming salts which are decomposed in the cold by carbonic acid. These salts oxidise slowly in the air, especially when their solutions are heated, forming a dark green substance, which dissolves in warm acids, the solution being red when viewed by transmitted light in thick layers, but green when in thin layers or when dilute. Alkalis change this to a fine purple. Glutazine is also a base, dissolving in cold dilute mineral acids without decomposition. Cold concentrated acids, except nitric, do not decompose it. On warming, the dilute nitric acid solution is oxidised; that in hydrochloric or sulphuric acids is decomposed into ammonia and, in the former case, trioxypyridine; in the latter, trioxypyridine anhydride. Its neutral solution gives, in the cold, with ferric chloride a deep red color, which, on warming, becomes dark green, remaining clear (characteristic). No pyridine was obtained by distilling with zinc dust.

The *hydrochlorate* is obtained by dissolving the body in cold concentrated hydrochloric acid. The salt at once crystallises out as colorless prisms, readily soluble in alcohol, but soluble without decomposition only in water containing free hydrochloric acid.

	Calculated for $C_5H_6N_2O_2.HCl + H_2O$.	Found.
Cl	19.67	19.54

It is permanent over sulphuric acid; but loses most of its water at 100°, a small part reacting to form ammonium chloride, etc.

The *sulphate* forms colorless prisms, moderately soluble in water containing free acid.

The *sodium*, *ammonium* and *barium* salts are extremely soluble in water, and could not be obtained pure, as they easily oxidise in the air, becoming green. The ammonium salt dissociates completely on boiling. The *silver salt* forms colorless leaflets, with much crystal water, which is lost on standing in the air. It is insoluble, and soon blackens in the light or on heating or boiling with water.

	Calculated for $C_5H_5O_2N_2Ag$.	Found.
Ag	46.35	44.61

Action of Bromine on Dioxyamidopyridine.

Dioxyamidopyridine gives a very characteristic reaction with bromine water. If a little of this reagent is added to its solution in dilute hydrochloric acid, a yellow crystalline precipitate is at once formed, which, on gently warming, becomes dark green. It also soon becomes green if exposed to the air, and hence is difficult to isolate. It dissolves in cold sodium hydroxide solution, and on acidifying crystallises out as prisms. Ammonia converts it into a white insoluble substance. It also dissolves in hot alcohol. The green substance is insoluble in water, alcohol, acids, or alkalis, but is instantly reduced by warming with stannous chloride, forming an insoluble yellow body, which again becomes green by warming with bromine water. These reactions have not been further studied. If bromine water is added to the acid solution *in excess*, till no further decolorisation occurs, the yellow body at first formed redissolves, and in a short time the solution becomes filled with colorless needles. These were several times recrystallised from chloroform and analysed. This serves to detect dioxyamidopyridine (and trioxypyridine) in quite dilute solutions.

	Calculated for $C_4H_2Br_5NO_2$.	Found.	
C	9.68	9.81	
H	.40	.56	
N	2.82	3.34	3.34
Br	80.64	81.99	79.82

Owing to its instability the substance is difficult to purify sufficiently for analysis, but its decompositions prove beyond doubt the formula $C_4H_2Br_5NO_2$. It forms beautiful colorless needles or prisms. Its fusing point, because of its instability, cannot be obtained constant; in the most favorable cases it was 148°, but often much lower. Heated higher it gives off bromine and hydrobromic acid. It is insoluble in cold water; readily in alcohol, which slowly decomposes it on heating; readily in ether and glacial acetic acid; moderately in cold, readily in hot benzene; moderately in hot chloroform, and insoluble in ligroin. It is instantly decomposed by alkalis, but is insoluble in cold dilute acids. It is best recrystallised from chloroform; but the solution, if allowed to stand too long, contains free bromine. Its nature is explained by its decomposition with water and alcoholic ammonia.

Some of the body was boiled with water in a flask provided with an inverted condenser, a current of air free from carbon dioxide being passed through, and into a flask of baryta water. On boiling, oil drops appeared in the liquid, and barium carbonate was formed in the baryta water. After about ten minutes' boiling the oil was drawn off, and found to have the odor and boiling point of *bromoform*, and gave the isonitrile reaction with aniline. The concentrated aqueous solution deposited crystals, which, after recrystallisation, fused at 154° and showed the other properties of *dibromacetamide* (m. pt. 156°).

	Calculated for $CHBr_2.CONH_2$.	Found.
C	11.06	11.42
H	1.38	1.48
N	6.45	6.80

Dibromacetamide sublimes readily without decomposition; is moderately soluble in cold, easily in hot water, alcohol, ether and chloroform. The body $C_4H_3Br_5NO_2$ is totally decomposed by boiling a minute with alcoholic ammonia. On cooling, crystals were deposited, which, after several recrystallisations from alcohol, formed octahedra fusing at 200.5° and agreeing with the description of *dibrommalonamide*, which fuses at 206°.[1] The yield was good.

	Calculated for $CBr_2(CONH_2)_2$.	Found.	
C	13.85	14.42	13.96
H	1.54	1.70	1.66
N	10.75	11.09	

It may be mentioned that dibrommalonamide has a persistent disagreeable sweet taste, accompanied by a sensation of irritation in the mouth and throat. The alcoholic ammoniacal solution contained bromoform and a small quantity of a body fusing at 100°–103°. These decompositions are easily explained, if we regard the body $C_4H_2Br_5NO_2$ as the *amide of pentabromacetacetic acid* (or pentabromacetylacetamide) $CBr_3.CO.CBr_2.CONH_2$.

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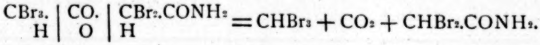
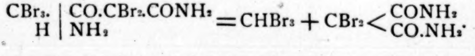
[1] Freund, Berichte **17**, 783.

I. With water—



$$\begin{array}{l|c|l} CBr_3. & CO. & CBr_2.CONH_2 \\ H & O & H \end{array} = CHBr_3 + CO_2 + CHBr_2.CONH_2.$$

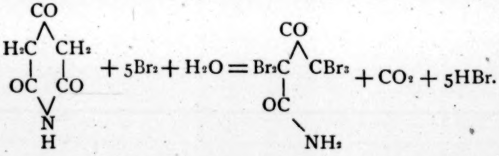
II. With alcoholic ammonia—



$$\begin{array}{l|l} CBr_3. & CO.CBr_2.CONH_2 \\ H & NH_2 \end{array} = CHBr_3 + CBr_2 < \begin{array}{l} CONH_2 \\ CO.NH_2 \end{array}.$$

The action of aqueous ammonia takes place in another direction, which was not studied.

Trioxypyridine, under similar circumstances, also gives pentabromacetylacetamide. We may therefore regard the action of bromine on dioxyamidopyridine as taking place thus, after separation of ammonia:



Action of Acetyl Chloride on Dioxyamidopyridine.

Dioxyamidopyridine and acetyl chloride readily react: best by heating in a sealed tube at 100°–120°. On cooling no hydrochloric acid escapes, and nothing is dissolved in the excess of the reagent. The product is a colorless crystalline mass, chiefly the hydrochlorate of *monoacetyldioxyamidopyridine.* It could not be recrystallised without partial decomposition, and was analysed after drying at 120°.

	Calculated for $C_5H_5(C_2H_3O)N_2O_2.HCl$.	Found.	
C	41.08	40.10	41.14
H	4.40	4.74	4.80
N	13.69	12.48	

It is readily soluble in alcohol, but is decomposed by water.

The free acetyl compound is obtained by decomposing the above salt by sodium acetate, and purified by recrystallising from water.

	Calculated for $C_5H_5(C_2H_3O)N_2O_2$.	Found.
C	50.00	49.58
H	4.76	4.96
N	16.67	16.42

Monoacetyldioxyamidopyridine closely resembles dioxyamidopyridine, but is somewhat less soluble in water and more soluble in alcohol. It crystallises from water in small lustrous plates, which, when pure, are colorless, but usually have a greenish tint. It begins to blacken at about 230°, and fuses at 285°–290°. Its solution gives no color in the cold with ferric chloride, or at most a faint brown. On boiling it becomes violet. It is difficultly soluble in acids, but readily in alkalis. It does not react with hydroxylamine. It is a monobasic acid. The *ammonium salt* crystallises from its solution in excess of warm ammonia in transparent hexagonal plates. It is moderately soluble in cold water, insoluble in alcohol, and on gently heating gives off water and ammonia.

	Calculated for $C_5H_4(C_2H_3O)N_2O_2.NH_4 + H_2O$.	Found.
C	41.38	41.86
H	6.40	6.66
N	20.69	20.56

The *barium salt* is easily soluble in water. The *silver salt* is insoluble and unstable.

The position of the acetyl has not been decided. The fact that bromine water does not give the colored products obtained from dioxyamidopyridine, which evidently depend on the presence of the imido group, and its neutrality towards hydroxylamine, make it probable that it replaces the imide hydrogen. It decolorises bromine water but slightly, and the product, fine needles, is not identical with pentabromacetylacetamide.

By boiling with acetic anhydride a higher acetyl derivative appears to be formed, which remains as a syrup on evaporating, from which nothing crystalline could be obtained. Alkalis decompose it instantly, giving the monoacetyl compound.

Action of Hydroxylamine on Dioxyamidopyridine.

Dioxyamidopyridine reacts readily with hydroxylamine, ammonia being split off and a monoxime formed, the reaction taking place equally in alkaline, neutral or acid solution. The oxime is readily obtained by heating a solution of dioxyamidopyridine to boiling with excess of hydroxylamine hydrochlorate. On cooling it crystallises out, and is pure after once recrystallising from water. It contains 1 mol. crystal water, which escapes slowly spontaneously, or rapidly by heating at 100°.

	Calculated for $C_5H_5O_2(NOH)N + H_2O$.	Found.
H_2O	11.25	11.56

The anhydrous substance gave—

	Calculated for $C_5H_5O_2(NOH)N$.	Found.
N	19.72	19.77

The crystallised oxime is a heavy, colorless sand, consisting of transparent hexagonal plates; on losing its water it becomes whiter. It blackens slowly above 150°, and fuses at 194°–196°, with sudden evolution of gas. It is difficultly soluble in cold, moderately in hot water, less soluble in alcohol, nearly insoluble in ether, and insoluble in chloroform. The aqueous solution soon becomes red. Ferric chloride gives in the cold no color; on warming, a brown, turbid solution. It dissolves in alkali and is reprecipitated by dilute acids, in which it is nearly insoluble. The alkaline solutions are often at first nearly colorless, but on standing or heating give various colors, depending on the nature and concentration of the alkali. Strong sodium carbonate solution gives a blue color, passing into brown and then red on heating. Very dilute ammonia gives a yellow-red solution, which, on warming, changes to a splendid purple, so intense that one milligram distinctly colors several litres of water. The oxime forms salts with mineral acids. It is insoluble in concentrated hydrochloric acid, which converts it into a salt crystallising in rhombic plates, soluble in alcohol, but decomposed by water. It loses its acid slowly at 90°.

	Calculated for $C_5H_5O_2(NOH)N.HCl$.	Found.
Cl	19.89	19.17

The oxime is readily decomposed by boiling with concentrated hydrochloric acid into hydroxylamine and trioxypyridine.

All attempts to introduce a second oximide group by long heating in neutral or slightly acid solution failed.

An analogous compound is formed with phenylhydrazine, with separation of ammonia. It will be described below. (See trioxypyridine.)

Action of Acids on Dioxyamidopyridine.

Weak acids, such as acetic, have no action on dioxyamidopyridine. It is readily oxidised by strong nitric acid in the cold, and by dilute nitric acid on warming. Boiling hydrochloric acid converts it into ammonia and *trioxypyridine;* boiling dilute sulphuric acid into ammonia and *trioxypyridine anhydride,* $C_{10}H_8O_5N_2$.

αα′γ-Trioxypyridine.—By boiling for 3—4 minutes with concentrated or moderately dilute hydrochloric acid, dioxyamidopyridine is completely decomposed according to the equation

$$C_5H_6O_2N_2+HCl+H_2O=C_5H_5O_3N+NH_4Cl.$$

An estimation of the ammonia formed showed that it contains one-half the total nitrogen of the body.

Calculated for 1 atom N.	Calculated for 2 atoms N.	Found.
11.11	22.22	10.71

The separation of the other product presents some difficulties. The following method was finally adopted:

Dioxyamidopyridine is boiled with excess of concentrated hydrochloric acid for 3—4 minutes, and the solution evaporated as quickly as possible on the water bath in large watch glasses. The quantity of dioxyamidopyridine to each watch glass should not exceed two grams, as otherwise the evaporation takes too long and secondary products are formed, which cannot be removed. The dry residue, after pulverising, is covered with cold absolute alcohol, which dissolves the trioxypyridine hydrochlorate readily, leaving the sal ammoniac. The alcoholic filtrate is quickly evaporated to a thick syrup on the water bath, in not too great quantities, as here, too, secondary products are formed. The thick syrup is diluted with about 2 parts water for each part glutazine, and a solution of caustic soda (.3 part for 1 part glutazine) in twice its weight of water added, with cooling. This should just decompose the hydrochlorate, without causing precipitation of sodium chloride, or holding too much trioxypyridine in solution. A thick mass of crystals soon forms, which is sucked out, pressed on a porous plate, washed on another plate with a little water, and dried. The product is yellowish, and should leave no ash.

	Calculated for $C_5H_5O_3N$.	Found. I.	Found. II.
C	47.24	46.37[1]	47.00
H	3.94	4.23	4.36
N	11.02	10.54	10.81

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[1] Analysis of a preparation not quite free from inorganic matter.

αα'γ-Trioxypyridine, thus prepared, is a heavy yellowish sandy powder, consisting of microscopic prisms or needles. Heated above 100° it slowly becomes yellower, and at 220°–230° swells up with only partial fusion, gives off water, and becomes orange-colored. When dry it is permanent, but when moist, and especially when heated in solution, it rapidly changes. It is moderately soluble in cold, readily in hot water, and insoluble in all other neutral solvents. It does not readily recrystallise from its concentrated aqueous solution, and cannot be purified in this way. On evaporating a brownish mass is obtained, containing unaltered trioxypyridine, its anhydride, $C_{10}H_8O_5N_2$, and other substances. With ferric chloride it gives a deep red color, which, on standing or warming, becomes yellow. Barium chloride and ammonia give no precipitate. These two reactions distinguish it from the trioxypyridine or pyromekazonic acid of Ost,[1] which gives an indigo-blue color with ferric chloride and a blue precipitate with the latter reagents. Bromine water gives no precipitate unless added in excess, when *pentabromacetylacetamide* (see above) is formed. Heated with zinc dust it carbonises for the greater part, the distillate containing ammonia and pyridine, which was recognised by its odor, but not obtained in quantity sufficient for separation and analysis.

Trioxypyridine has a strong acid reaction, and decomposes carbonates in the cold, giving salts which are not decomposed by carbonic acid. It appears to be monobasic. The alkaline and earthy salts are very soluble in water, and their solutions soon become dark green in the air.

The *ammonium salt*, obtained by evaporating its ammoniacal solution in a vacuum over sulphuric acid, forms thick prisms, which could not be obtained colorless. The *barium salt* was obtained and analysed in solution only by dissolving a known weight of trioxypyridine in baryta water, precipitating excess by carbonic acid and estimating barium in the filtrate.

	Calculated for $(C_5H_4O_3N)_2Ba$.	Found.
Ba	35.22	36.02

The *silver salt* is insoluble and unstable. The *hydrochlorate* forms needles easily soluble in water and alcohol, and partially decomposing on evaporation into ill-defined products.

Trioxypyridine has decidedly the properties of a ketone, as shown by its reaction with hydroxylamine, phenylhydrazine and ammonia. On warming with hydroxylamine hydrochlorate it gives an oxime fusing at 194°-196°, and in every respect identical with that obtained from dioxyamidopyridine, which was confirmed by analysis.

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[1] Jour. pr. Chem. [2] **19**, 204; **27**, 258.

	Calculated for $C_5H_5O_2(NOH)N + H_2O$.	Found.
H_2O	11.25	11.22

	Calculated for $C_5H_5O_2(NOH)N$.	Found.
N	19.72	19.80

Phenylhydrazine Derivative.

To obtain this it is not necessary or desirable to isolate the trioxypyridine. One part dioxyamidopyridine is decomposed by boiling with hydrochloric acid, and to the diluted solution one part phenylhydrazine and sodium acetate are added. The body crystallises out at once, and may be recrystallised from alcohol.

	Calculated for $C_5H_5O_2(N_2HC_6H_5)N$.	Found.
N	19.35	19.75

It may also be obtained directly from dioxyamidopyridine, ammonia being evolved. It forms colorless plates closely resembling glutazine. It begins to blacken at 220° and fuses at 230°, with violent evolution of gas. It is difficultly soluble in hot water, difficultly in cold, readily in hot alcohol, scarcely soluble in dilute acids, readily in alkalis.

Formation of Dioxyamidopyridine from Trioxypyridine.

If fused with excess of crystallised ammonium acetate for 3—4 minutes at 120°-140°, trioxypyridine is quantitatively converted into dioxyamidopyridine, which remains, on adding alcohol, as a greenish powder, giving the characteristic reactions with ferric chloride and bromine water. After recrystallising it was analysed.

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.33

The synthesis cannot be effected by simply evaporating with ammonia.

Trioxypyridine Anhydride.

This is the chief product of the decomposition of dioxyamidopyridine with boiling dilute sulphuric acid, and is best isolated as its acid barium salt. It is very stable, and may be prepared in any quantity in one operation. Dioxyamidopyridine is boiled for five minutes with twenty parts of ten per cent. sulphuric acid, the hot solution supersaturated with concentrated baryta water, filtered from barium sulphate, and boiled until the ammonia is driven off, which should be done in a flask, as otherwise partial oxidation occurs. The solution, containing the neutral barium salt and free baryta, is slightly acidified with acetic acid, which throws down the acid salt, and left to stand a few hours until the crystallisation is complete. The product is purified by twice dissolving in baryta water and precipitating with acetic acid. The *acid barium salt* thus obtained forms a yellow precipitate, or, when obtained from dilute solutions, groups of small yellow prisms. It is insoluble in water, alcohol and dilute acetic acid, but is decomposed by mineral acids, and dissolved by alkalis. It contains four molecules crystal water, two of which escape over sulphuric acid, the other two only on heating to 180°.

	Calculated for $(C_{10}H_7O_5N_2)_2Ba + 4H_2O$.	Found.		
$2H_2O$	5·30	5·37	5·33	5·38
$2H_2O$	5·30		5·38	
Ba	20.18	20.04	20.14	
N	8.25	8.14		

To isolate the anhydride, the acid barium salt is boiled with excess of concentrated hydrochloric acid, evaporated to dryness on the water bath, again moistened with concentrated acid, and dried. The pulverised residue is covered with absolute alcohol, which dissolves the hydrochlorate, leaving barium chloride. The alcoholic solution is evaporated, a little water added, and again evaporated, and this is repeated three or four times, or until no more hydrochloric acid is given off. The crystalline residue is boiled with a little water, which removes a greenish impurity.

	Calculated for $C_{10}H_8O_5N_2$.	Found.	
C	50.85	50.05	50.62
H	3·39	3·56	3·73
N	11.86	11.86	11.98

Trioxypyridine anhydride, thus prepared, is a loose mass of flesh-colored microscopic prisms. It is very stable, and fuses only at high temperature, with decomposition. It dissolves but slowly in boiling water, and is insoluble in other neutral solvents and in glacial acetic acid. It is readily soluble only in excess of alkali baryta water, or alkaline carbonates, which it decomposes in the cold. It dissolves difficultly in concentrated hydrochloric acid forming the *hydrochlorate*, which is soluble in alcohol and crystallises in needles, but is decomposed by water, forming a jelly which loses all its acid on evaporating, leaving it in the crystalline form. The *sulphate* also forms needles, and is similarly decomposed by water. Its power of gelatinising is very great, and is due to the presence of its own or other salts, which must be removed before it can crystallise. In the pure state it does not gelatinise, but separates from its solution in hot water as small prisms. The jelly does not crystallise by long standing. Under some circumstances it is partly precipitated as an amorphous flocculent mass.

The *acid sodium salt* forms yellow prisms, rather more soluble than the corresponding barium salt.

The *acid ammonium salt* forms yellow crystals, difficultly soluble in cold water.

The *acid silver salt* is insoluble.

None of these are decomposed by acetic acid.

The *neutral* alkaline and earthy salts have the formulas $C_{10}H_6O_5N_2M'_2$ and $C_{10}H_6O_5N_2M''$ and are easily soluble in water, the solution gradually oxidising in the air. They are not decomposed by carbonic acid ; acetic acid throws down the acid salt.

The *neutral barium salt* is difficult to obtain pure in solid form. Its solution, obtained by dissolving a known weight of anhydride in baryta water, precipitating excess by carbonic acid, and determining barium in the filtrate, gave

	Calculated for $C_{10}H_8O_5N_2Ba$.	Found.
Ba	36.81	36.93

The *neutral silver salt* is insoluble.

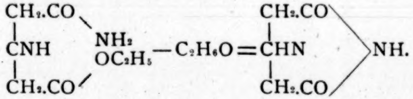
No salts containing more metal could be obtained.

Trioxypyridine anhydride reacts under no conditions with hydroxylamine. An imido group could not be introduced by fusing with ammonium acetate, which gives simply the acid ammonium salt. Phenylhydrazine does not act on it in the cold ; on boiling, a red substance soluble in alkali was obtained.

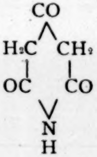
Bromine water produces a precipitate of flesh-colored needles, not decomposed by boiling water. The anhydride cannot be decomposed into trioxypyridine by boiling with acids or alkalis, but is formed from it by evaporating its aqueous solution.

Constitution of the Above Bodies.

From its formation from β-imidoglutamic ethyl ester the two oxygen atoms of dioxyamidopyridine must occupy the αα'-, and the amido or imido group the γ-position.



Whence follows the symmetrical αα'γ arrangement for trioxypyridine, which is therefore the analogue in the pyridine series of phloroglucine, dioxyamidopyridine being the analogue of phloramine. The ease with which the γ-oxygen reacts with hydroxylamine, phenylhydrazine and ammonia proves beyond doubt that it exists in the ketone form, which is confirmed by the studies of Haitinger and Lieben[1] on the derivatives of γ-oxypyridine. Whether the αα'-oxygen atoms exist as carbonyl or hydroxyl is not so readily decided. Their neutrality towards hydroxylamine cannot be regarded as proof of the latter view, as the group C—CO—NH is not known to react with it. If we assume that von Baeyer's[2] theory that rings tend to be purely secondary or purely tertiary holds in this case, and remember that α-oxypyridine is a lactam,[3] the presumption is in favor of the formulas



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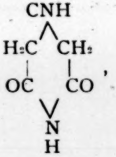

and the bodies should be designated as *αα'γ-triketopiperidine* and *αα'-diketo-γ-imidopiperidine.*[4] Whether these bodies ever assume the tertiary form is questionable. The neutrality of trioxypyridine anhydride towards hydroxylamine and fused ammonium acetate may indicate the absence of the, in other cases, so easily reacting γ-carbonyl group, and that a change to the phenol form with anhydride formation has occurred, giving

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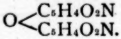
[1] Monatshefte **6**, 298.

[2] Berichte **19**, 162.

[3] Von Pechmann, Berichte **18**, 317.

[4] Von Baeyer, Berichte **19**, 161-163.



$$O<\begin{matrix}C_5H_4O_2N\\C_5H_4O_2N.\end{matrix}$$

As to whether the α- or γ-oxygen atoms are here concerned it is useless to speculate. No salts of glutazine or trioxypyridine containing more than one atom of metal in the molecule could be obtained, and this might well be associated with the pyridine nitrogen. Attempts to obtain alkyl derivatives, whose solubility or insolubility in alkalis, and possible decomposition into alkylamine by reducing agents,[1] might throw light on the subject, have not been pursued far enough to yield definite results. The silver salt of glutazine gives with ethyl iodide only a small quantity of an easily fusible body, insoluble in alkalis—probably the monoethyl ether. Considering the doubt which pertains to the subject, we have retained the older names trioxy- and dioxyamido-pyridine, not wishing thereby to commit ourselves to any decided view of the constitution of these bodies further than that indicated by the experiments above given.

Chlorine Derivatives of γ-amidopyridine.

With phosphorus pentachloride, dioxyamidopyridine yields at least four well-marked products—viz.:

1. Dichlordioxyamidopyridine, $C_5N_2H_4Cl_2O_2$.
2. Trichloroxyamidopyridine, $C_5N_2H_3Cl_3O$.
3. Trichloramidopyridine, $C_5N_2H_3Cl_3$.
4. Tetrachloramidopyridine, $C_5N_2H_2Cl_4$.

Under the conditions observed 2 and 4 were formed in large and nearly equal quantity, while the amount of 1 and 3 was very small. Monochloroxy- or dichloramido-pyridine could not be obtained. An attempt to make them by using phosphorus trichloride also led to no result.

Dioxyamidopyridine is made into a thin paste with phosphorus oxychloride, and 6—7 parts phosphorus pentachloride gradually added. When the reaction has moderated, the flask, provided with a return condenser, is heated in an oil bath for two or three hours, or until the contents form a nearly clear liquid. The oxychloride and unchanged pentachloride are then distilled off until the residue is nearly solid and the temperature of the oil about 200°–210°. Water is then added, with cooling, and the flask is left to stand until all residual oxychloride is destroyed. Bodies 2 and 4 are found mostly in the insoluble residue, and are separated by boiling with dilute alkali, which dissolves 2 only, which is then precipitated by an acid. Both are purified by several recrystallisations from alcohol. The acid filtrate from the mixture of 2 and 4, on being made alkaline, gradually deposits 3, which is recrystallised from much hot water. The alkaline filtrate, on adding acetic acid, gives needles, which may consist of 1 alone or of 1 and 2, which may be separated by dilute hydrochloric acid, in which 1 is more soluble. It is then recrystallised from water.

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[1] Von Pechmann, Berichte **18**, 317.

Whether these bodies contain the amido or imido group remains uncertain. We have provisionally assumed the former, or tertiary form, which best agrees with the properties of body 2.

Dichlordioxyamidopyridine, $C_5N_2H_4Cl_2O_2$.

	Calculated for $C_5N_2H_4Cl_2O_2$.	Found.
Cl	36.41	35.79
N	14.36	14.36

The body, recrystallised from water, forms short, flat, colorless needles, fusing, with decomposition, at 241.5°. It is difficultly soluble in hot water and alcohol, readily in alkalis or dilute hydrochloric acid. It slowly decolorises bromine water, giving a precipitate of colorless stars, soluble in boiling water. Of its constitution nothing is known except that the oxygen atoms have the $\alpha\alpha'$-, the amido or imido group the γ-positions.

Trichloramidopyridine, $C_5N_2H_3Cl_3$.

	Calculated for $C_5N_2H_3Cl_3$.	Found.
Cl	53.92	53.93
N	14.18	14.49

The body, recrystallised from hot water, in which it is difficultly soluble, forms a felt-like mass of long, delicate, colorless needles. It fuses at 157.5°, and readily sublimes unchanged. It is very soluble in alcohol, slightly in dilute hydrochloric acid, and insoluble in alkali. It is characterised by its dilute solution giving, with bromine water, a precipitate, which, after recrystallising from alcohol, forms flat colorless needles, fusing at 223°, easily sublimable and insoluble in water, acids and alkalis; probably monobromtrichloramidopyridine. The chlorine atoms must occupy the $\alpha\alpha'\beta$-positions.

Trichloroxyamidopyridine, $C_5N_2H_3Cl_3O$.

	Calculated for $C_5N_2H_3Cl_3O$.	Found.	
C	28.10	28.09	
H	1.41	1.64	
N	13.11	13.61	
Cl	49.88	50.33	50.48

The body forms flat colorless needles. It fuses at 282°, and by careful heating may be sublimed unchanged. It is almost insoluble in cold, very slightly in hot water; difficultly in cold, moderately in hot alcohol; moderately in ether; difficultly in hot benzene; insoluble in ligroin. It dissolves readily in strong hydrochloric or sulphuric acids, and is in greater part precipitated by diluting. The little remaining in solution can be extracted by ether. With ferric chloride it gives a red color only on boiling. It is not attacked by boiling with concentrated alkalis or acids, but by fusion with alkali or by heating to a high temperature with fuming hydrochloric or hydriodic acids; in the latter case the only well-marked products are carbon dioxide and ammonia. It is not acted on by hydroxylamine or bromine water. It dissolves in pure phenylhydrazine without change, but, on boiling, ammonia is evolved. Phosphorus pentachloride at 150° slowly converts it into tetrachloramidopyridine. It is also formed in small quantity by heating β-imidoglutamic ethyl ester with phosphorus pentachloride. It is a monobasic acid, decomposing soluble carbonates on gently warming. The salts are decomposed by acetic acid.

The *sodium salt* forms needles with 3—4 molecules crystal water, moderately soluble in cold water, difficultly in alcohol.

Dried at 100° it gave:

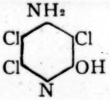
	Calculated for $C_5N_2H_2Cl_3ONa$.	Found.
Na	9.77	10.35

It forms anhydrous hair-like tufts by mixing the alcoholic solution of the free body with alcoholic sodium ethylate.

Its solution gives: with *barium chloride*, at first nothing; on standing or warming, prisms difficultly soluble in hot water; with *lead acetate*, an amorphous white precipitate; with *silver nitrate*, a flocculent precipitate, or sometimes a firm, transparent jelly.

The *ammonium salt* is completely dissociated on evaporating.

The properties of the ethyl ether of trichloroxyamidopyridine render probable the phenol form, whence the formula



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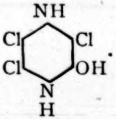
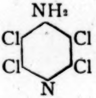


Tetrachloramidopyridine,



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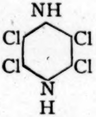

	Calculated for $C_5N_2H_2Cl_4$.	Found.
C	25.86	26.11
H	.86	1.08
N	12.07	12.34
Cl	61.21	61.39

The body forms colorless thin leaflets or nearly cubical crystals. It fuses at 212°, and sublimes without decomposition. It is insoluble in water; difficultly in cold, moderately in hot alcohol, but more so than trichloroxyamidopyridine; soluble in hot benzene. It is insoluble in alkalis, and nearly so in hot hydrochloric acid, strong or dilute. It dissolves in cold concentrated sulphuric acid, with which it may be boiled without decomposition. Alkalis attack it only on fusion.

Fuming hydriodic acid reduces tetrachloramidopyridine, giving a mixture of substances with pyridine-like odor and properties which give Hofmann's reaction.[1] In no case could complete reduction be effected. Heated in sealed tubes with fuming hydriodic acid for ten hours at 200° black needles of an iodine addition product were obtained, fusing under 80°. On dissolving in sulphurous acid and making alkaline, colorless needles were obtained, which were readily soluble in dilute acids, moderately soluble in hot water, and volatile with steam or at 100°, the vapor

[1] Berichte **17**, 1908.

having a rather faint pyridine-like odor. After recrystallising they fused at 157.5°. The recrystallised product was distilled with steam and collected in two fractions, each of which fused at 158°. A chlorine determination gave 43.32 per cent.; calculated for a dichloramidopyridine, 43.56 per cent. It gave a chloroplatinate crystallising in needles, difficultly soluble in water and decomposing without fusion. It contained crystal water, which escaped at 100°.

	Calculated for $(C_5H_2Cl_2(NH_2)N.HCl)_2PtCl_4$.	Found.
Pt	26.73	26.73

Unfortunately, not enough of the substance to confirm these results could be obtained. Its pyridine-like odor is in favor of its being simply impure dichlorpyridine. The filtrate from these crystals contained still further reduced products of intense pyridine odor.

On heating tetrachloramidopyridine with 10 parts fusing hydriodic acid, and some red phosphorus for sixty hours at 300–350°, and treating the product as above, nothing crystalline could be obtained. The distillate, a clear liquid of intense pyridine odor, was acidified with hydrochloric acid and evaporated, whereby partial dissociation occurred. The residue was extracted with cold absolute alcohol, which left much ammonium chloride. Again evaporating and extracting, a syrupy salt was obtained, a portion of which gave an oil of intense pyridine odor on dissolving in concentrated alkali. The chloroplatinate from this, after recrystallising, formed flat and apparently homogeneous prisms, resembling those of pyridine chloroplatinate, but which fused at 235–245° (the pyridine salt fuses at 236°). The quantity sufficed for but one analysis.

	Found.	Calculated for $(C_5H_5N.HCl)_2PtCl_4$.	Calculated for $(C_5H_4ClN.HCl)_2PtCl_4$.
Pt	33.50	34.41	30.60

The oil is therefore probably a mixture of pyridine with chlorpyridine. In no case was any tetrachloramidopyridine recovered. The first stages of the reduction are easy, the last very difficult.

Unfortunately it was not possible to pursue the experiments further on a scale admitting of isolating the various reduction products, but the results prove beyond doubt the pyridine nature of the whole class of bodies under consideration.

Ethers of Amidopyridine.

Tetrachloramidopyridine, boiled with excess of sodium ethylate and absolute alcohol for two hours, is entirely converted into a new compound, in which one chlorine atom is replaced by ethoxyl. The product is poured into water, the precipitated crystals distilled with steam, dissolved in a little alcohol, and precipitated by water.

	Calculated for $C_5N_2H_2Cl_3(OC_2H_5)$.	Found.	
C	34.78		35.30
H	2.90	3.12	3.17
Cl	44.10	44.20	

Trichlorethoxyamidopyridine forms colorless needles fusing at 83° and subliming unchanged. It is easily volatile with steam, and slightly at ordinary temperatures, its vapor having a characteristic, sharp, but agreeable aromatic odor. It is insoluble in water, alkalis and dilute acids; extremely soluble in alcohol, ether, benzene and chloroform; moderately in ligroin. Heated in a sealed tube with dilute hydrochloric acid (sp. gr. 1.15) at a little over 100° it is readily decomposed into ethyl chloride and the trichloroxyamidopyridine above described (m. pt. 282°).

If the anhydrous sodium salt of trichloroxyamidopyridine is heated with one equivalent of ethyl iodide and absolute alcohol at 120°, two substances are formed, one of which, not volatile with steam, was not further examined. The other, after distilling with steam, fused at 83°, and was in every respect identical with the above ethoxyl compound.

The formation of the same ether from tetrachloramidopyridine and sodium ethylate, and from a salt of trichloroxyamidopyridine and ethyl iodide, proves that in this case, as in others, the atom occupying the α-position reacts most readily. The low temperature at which these reactions occur (80° and 120° respectively, and probably lower), taken with the ease with which the ether is decomposed by dilute hydrochloric acid, renders it probable that no transference of atoms occurs, and, therefore, that trichloroxyamidopyridine and its ether contain hydroxyl and ethoxyl respectively.

Tetrachloramidopyridine is further acted on if heated with excess of sodium ethylate and absolute alcohol for 3—4 hours at 190°. The liquid, on cooling, contains crystals of sodium chloride and needles. The whole is poured into water, whereby the crystals dissolve and others appear. Without removing these, the alkaline liquid is shaken out two or three times with ether, which extracts a substance which may be purified by distilling with steam, dissolving the distilled crystals in alcohol and precipitating with water (Body A). The alkaline liquid, after extraction, is acidified with hydrochloric acid, and with deposited crystals again extracted three or four times with ether. The ether contains a body (B) which may be purified by recrystallising from very dilute alcohol. The yield of A and B was nearly equal.

Body A.

	Calculated for $C_5N_2H_2Cl_2(OC_2H_5)_2$.	Found.
C	43.02	42.40
H	4.78	5.04

Dichlordiethoxyamidopyridine forms long, colorless, flat needles, fusing at 98°, readily sublimable and volatile with steam, the odor of its vapor closely resembling that of trichlorethoxyamidopyridine. It is insoluble in water, alkalis and dilute acids; very soluble in alcohol and ether. It gives a red color on boiling with ferric chloride.

Body B.

	Calculated for $C_5N_2H_2Cl_2(OH)(OC_2H_5)$.	Found.
C	37.67	37.54
H	3.59	3.68

Dichloroxyethoxyamidopyridine forms colorless, brittle, flat needles, fusing at 161.5°, and subliming if carefully heated. It is difficultly soluble in hot water, readily in alcohol and ether. It is not volatile with steam. It is insoluble in dilute acids, but dissolves in alkalis, forming salts, of which the *sodium salt* forms lustrous rhombic plates rather difficultly soluble in cold water and decomposed by acetic acid.

The same compound is formed by heating trichloroxyamidopyridine with sodium ethylate and absolute alcohol[1] for three or four hours at 190°. Moreover, the diethoxy compound, by heating several hours with sodium ethylate and absolute alcohol at 190°, is almost completely converted into the oxyethoxy compound. Hence, as regards the positions of these groups, in the one case the hydroxyl, in the other one ethoxyl, occupies the α-position. The position of the other group could not be determined. Attempts were made to decompose the diethoxy body by hydrochloric acid, hoping to obtain the dichlordioxyamidopyridine of m. pt. 241.5°, thereby proving that the second α-chlorine atom is attacked. Experiments with acid of sp. gr. 1.14, at temperatures from 100° to 140°, showed that at the higher temperatures the body was totally decomposed into ethyl chloride, ammonia and amorphous products. At 100°–110° ethyl chloride and ammonia were also formed, but the body was largely unaltered, no dichloroxyethoxy- or dichlordioxy-amidopyridine could be detected. This, however, proves nothing, as the firmness with which the amido or imido group is held in all these cases is evidently proportional to the amount of chlorine, and it is possible that those bodies with but two atoms of chlorine may be nearly as easily decomposed by hydrochloric acid as is dioxyamidopyridine itself, and therefore would be destroyed as soon as formed.

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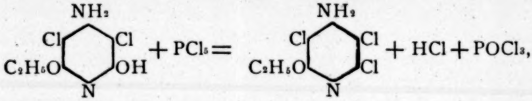
[1] This method of preparation is not to be recommended, for the decomposition is apt to go too far, or else some trichloroxyamidopyridine remains unacted on, and is not easily separated from the oxyethoxy compound.

An attempt to prove the α-position of the second ethoxy group, by heating the oxyethoxy compound with phosphorus pentachloride, thus obtaining the trichlorethoxyamidopyridine above described (m. pt. 83°), according to the equation



failed. The substance obtained resembled in odor and other properties the desired body, but fused at 175°. Considering the possibilities lying in a lactam and lactim structure, this can hardly be regarded as a *disproof* of the assumption, which must therefore be left at present undecided.

Von Baeyer's Laboratory, Munich, *August* 4, 1886.

Contributions from the Chemical Laboratory of Wesleyan University.

III.—ON THE LIBERATION OF NITROGEN FROM ITS COMPOUNDS AND THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.

By W. O. Atwater.

Experiments on the question of the assimilation of atmospheric nitrogen by plants are ordinarily made by comparing the amounts of nitrogen supplied in seed and fertilising materials with that found at the end of the experiment in the plants and in the soil or nutritive solution. If any nitrogen is found at the end of the experiment in excess of that supplied, the inference is that the excess must have come from the ambient air.

Such experiments are, however, exposed to an error resulting from the liberation of nitrogen from its compounds contained in the seed, the plant, or the food supplied. The effect of any such escape of nitrogen will be to reduce the quantity found at the end of the experiment. While, therefore, a gain is positive proof of the acquisition of nitrogen from the air, either directly by the plant through its foliage or indirectly through the medium in which the roots develop, the failure to find such acquisition is only negative proof of its non-occurrence.

In a previous communication,[1] to which this and the preceding one are supplementary, account was given of experiments by myself with peas grown in sand and supplied with certain quantities of nitrogen and other essential elements of plant food in nutritive solutions. In order to test the effect of abnormal conditions, the solutions in some of the experiments were made much more concentrated than experience has indicated to be favorable for assimilation. In some cases, furthermore, the total food-supply was made small in relation to the estimated demands of the plants, while in others it was more liberal. The quantity of nitrogen in the solutions was likewise varied, the quantity of mineral food remaining the same. Of the trials in concentrated solutions, one showed a small loss and the rest more or less gain of nitrogen. In the experiments in the moderately dilute solutions, the poorly fed plants obtained over one-third, and the tolerably well-fed ones one-half of their nitrogen from the atmosphere. It was remarked that the only considerable source of error in the experiments seemed to be in a probable loss of nitrogen by the decomposition of the nitrogen compounds of either the seeds (or plants) or the nutritive solutions, or both. It was in the hope of getting light upon this question of the loss of nitrogen that the work detailed in the previous article[1] was undertaken. The purpose of the present article, which, like the one last named, is really a continuation of the first one above referred to, is to indicate the bearing of the facts elicited upon my own and other experiments on the acquisition of atmospheric nitrogen.

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[1] This Journal **6**, 365.

INFLUENCE OF VARYING CONDITIONS UPON THE APPARENT ACQUISITION OF NITROGEN.

It will facilitate the discussion if some of the principal data which were given in detail in the first article are put together in such a manner as to show the quantities of nitrogen supplied and found, and the gain or loss under different conditions. This is attempted in Tables I and II.

TABLE I.

Statistics of Experiments on the Assimilation of Atmospheric Nitrogen by Peas.

Conditions of Experiments.			No. of Experiment.	Nitrogen supplied.			Nitrogen found at End of Experiment.			Apparent Gain + or Loss — of Nit'g'n
				In seeds.	In Nutritive Sol'n.	Total.	In Plants.	In Residual Solut'n.	Total.	
				Mgm.	Mgm.	Mgm.	Mgm.	Mgm.	Mgm.	Mgm.
Larger Nitrogen Ration.	Concentrated Solution.	Scantily fed.	8	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
		Well fed.	6	34.8	136.9	171.7	149.6	1.2	150.8	— 20.9
	Dilute Solution.	Scantily fed.	12	68.8	136.9	205.7	260.2	45.7	305.9	+100.2
		Well fed.	10	34.6	136.9	171.5	277.8	35.7	313.5	+142.0
Smaller Nitrogen Ration.	Concentrated Solution.	Scantily fed.	7	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
		Well fed.	5	34.2	59.4	93.6	156.1	0.0	156.1	+ 62.5
	Dilute Solution.	Scantily fed.	11	72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
		Well fed.	9	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2

The plants were grown in sand, supplied with solutions of appropriate salts including nitrogen in nitrates, and kept in open air, but protected from rain and dew. The experiments were in two series, one in each of two successive years. The second series included twelve experiments, of which Nos. 5–12 in the table suffice to illustrate the principal results obtained in the two series. The "concentrated" solutions contained from 2.5 to 6, and the "dilute" from 0.8 to 1.6 parts of water-free salts in 1000. A concentration of 1 per 1000 has elsewhere been found favorable, and one of over 2 per 1000 unfavorable to normal assimilation. The "well-fed" plants had quantities of mineral food estimated to be sufficient for their nourishment, the scantily fed ones one-half as much. The "larger nitrogen ration" was estimated to supply an amount of nitrogen rather small in proportion to the mineral food, and the "smaller nitrogen ration" less than one-half as much as the larger. The gain or loss of nitrogen is computed by adding to the amount of nitrogen in the plants that left in the nutritive solution at the end of the experiment, and subtracting from their sum the sum of the amounts in the seed and in the nutritive solution at the start. The figures for "apparent gain or loss" represent, therefore, the quantities acquired from the air less whatever may have been liberated from solution or seed or plants during growth. The nutritive solution and seed together contained from 94 to 212 mgm. and the plants from 116 to 278 mgm. of nitrogen in each experiment.

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[1] This Journal **8**, 327.

TABLE II.

Comparison between Apparent Gain or Loss of Nitrogen and Nitrogen Left in Nutritive Solution at End of Experiment, with Concentrated and Dilute Solutions.

Conditions of the Experiment.		No. of Experiment.	Residual Nitrogen in Solution. Estimated in per cent. of Total Nitrogen in the Solution.	Apparent Gain +, or Loss −, of Nitrogen. Estimated in per cent. of Total Nitrogen in the Plants.
With Larger Nitrogen Ration.			Per cent.	Per cent.
Concentrated Solutions	Scantily fed.	8	9.3	+ 1.5
	Well fed.	6	0.9	− 14.0
Dilute Solutions	Scantily fed.	12	33.4	+ 38.1
	Well fed.	10	26.1	+ 51.1
With Smaller Nitrogen Ration.				
Concentrated Solutions	Scantily fed.	7	0.0	+ 17.2
	Well fed.	5	0.0	+ 40.0
Dilute Solutions	Scantily fed.	11	4.5	+ 38.7
	Well fed.	9	2.4	+ 50.0

The figures bring out very clearly the facts stated above, that in every case in which the nutritive solution was as dilute as has been found favorable for normal growth, the plants contained a large quantity of nitrogen in excess of that supplied by nutritive solution and seed—a gain which must of course have come from the air—while in cases in which, as a test of the effect of abnormal conditions, the solutions were more concentrated, there was uniformly less gain, and in one case a loss, of nitrogen. In the last case nitrogen had evidently escaped. It was natural to infer that a similar liberation of nitrogen might have occurred in the other trials with concentrated solutions. This would help to explain the small gain of nitrogen in these cases, though another cause might be sought in decreased assimilation under this abnormal condition.

A curious result of the experiments, and one which can hardly be without significance, becomes apparent when the quantities of nitrogen left in the nutritive solutions at the end of the experiments are compared with each other and with the amounts apparently acquired from the air under different conditions, as is done in Tables II and III.

The conditions most favorable for growth were with the larger nitrogen ration in the dilute solutions, experiments Nos. 12 and 10. In each of these the plants contained so much nitrogen as to show that they must have acquired large quantities from the air, and yet they left large amounts behind in the nutritive solutions. The most abnormal conditions were those of the greatest concentration—to wit, those with the larger nitrogen ration in the concentrated solutions—*e. g.*, experiments Nos. 8 and 6. In these the plants contained so little nitrogen as to make in one case a very small gain, and in the other a positive loss. In each of these latter cases, there was very little or no residual nitrogen in the solutions at the end of the experiments. In other words, in the cases in which the plants contained the most nitrogen, namely, in the normally dilute solutions, they left the most behind; but where conditions were abnormal, in the concentrated solutions, they contained the least nitrogen and left the least behind.

The cases just named were with the larger nitrogen ration. With the smaller quantities of nitrogen the differences were in the same general direction, but less marked, as may also be seen in Table II. The plants seem to have used up the smaller stock of nitrogen more quickly, or at any rate more completely, than the large stock.

The matter will be still clearer if we examine the nitrogen statistics in the cases where the differences are most marked, Nos. 6 and 10, using the original data,[1] as is done in Table III.

TABLE III.

Comparative Nitrogen Statistics of Experiments in Concentrated and Dilute Solutions.

	Expt. No. 6. Concentrated Solution.	Expt. No. 10. Dilute Solution.
	Milligrams.	Milligrams.
Nitrogen supplied in nutritive solutions	136.9	136.9
Nitrogen supplied in seed	34.8	34.6
Total nitrogen supplied	171.7	171.5
Nitrogen left in nutritive solution	1.2	35.7
Total nitrogen removed by plants and otherwise	170.5	135.8
Nitrogen contained in plants	149.6	277.8
Apparent loss —, or gain +, of nitrogen	— 20.9	+ 142.0

Or, to put it in another way:

	Under Abnormal Conditions of Growth.	Under Normal Conditions of Growth.
There were placed at the disposal of the plants.	172 mgm. N.	172 mgm. N.
The plants in some way obtained[2].	150 " "	278 " "
The plants left behind unused.	1 " "	36 " "

Grown under favorable conditions, the plants contained at maturity (278 — 172) 106 milligrams more of nitrogen than the total amount supplied, and yet left 36 milligrams behind in the nutritive solution. Grown under abnormal conditions of concentration, the plants had (172 — 150) 22 milligrams less than was furnished, and yet only left 1 milligram behind.

Comparing Nos. 8 and 12, in which the conditions of growth are similarly, though less widely, diverse, we find precisely similar, though less marked, differences of result. So with Nos. 7 and 11 and Nos. 5 and 9, where the smaller quantities of nitrogen supplied make the differences in condition less, though still analogous, the differences in result are less, but of exactly the same tenor. In other words, the plants in the more dilute solutions contained the most nitrogen, evidently got the most from the air, and, at the same time, apparently drew the least from the solutions, while those in the concentrated solutions evidently got the least from the air, had the least when mature, but yet appeared to draw most heavily upon the store in the nutritive solution.

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[1] See detailed tables in former article, above referred to, this Journal **6**, 365.

[2] *I. e.*, they contained at maturity.

That these circumstances should be entirely fortuitous, and any inferences from them fanciful, is hardly to be believed. Granting them a meaning, it can be easily explained by supposing that there was some agency at work in the experiments with concentrated solutions setting nitrogen free, and that the agency in question, be it electricity, microbes, or something else, is less effectively resisted by the plants grown in abnormal than by those in normal conditions. This accords with the fact that higher organisms resist disease, including forms commonly attributed to microbes, the more effectively in proportion as they are well nourished and in otherwise healthy condition.

But if nitrogen escaped in the trials with concentrated solutions, may it not have escaped to some extent in the other cases also? If so, the results are all inaccurate as indications of the actual acquisition of atmospheric nitrogen, and the plants must have really obtained quantities larger, by the amounts thus liberated, than the figures imply.

The data and considerations in the previous article suggest two ways in which the nitrogen might have been lost: decomposition of the nitrogenous compounds of the seeds and plants, and decomposition of the nitrates of the nutritive solutions.

In the second, third and fourth series of the experiments by Mr. Rockwood and myself on the loss of nitrogen, described in the previous article, we attempted to make the conditions as similar as practicable to those of the assimilation experiments in question, except that no food was supplied to the plants. The loss of nitrogen in the experiments of the series in which the period of growth was longest, from 14 to 52 days, was from 10 to 15 per cent. of the nitrogen of the seed.[1]

In the experiments of Boussingault,[2] referred to in the previous article, seeds of beans and maize were caused to germinate in presence of nitrates under conditions analogous to those of my assimilation experiments, and 45.3 per cent. of the nitrate was estimated by him to have been liberated during a period of 21 days. With maize the loss of nitrogen was still greater. Since there were positive indications of loss in some of my experiments, and we have instances of its occurrence under more or less analogous conditions in the experiments just cited and in numerous others described in the last article, and since we have in the facts of decomposition and decay, with or without the agency of microbes, as illustrated in the article referred to, a clear explanation of the liberation of nitrogen, there can be hardly any reasonable doubt that such loss did occur in my experiments. But granting such loss, could it have been large enough to materially affect the quantity of nitrogen found at the end, and hence the apparent results of the experiments?

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[1] See Table III of previous article, Expts. 8, 11 and 13.

[2] Ann. Chim. Phys. [5], **22**, 1881, 433.

Neither Boussingault's results nor ours, above cited, give any measure whatever of the loss that may have been induced by like causes in the experiments now under discussion. But, in lack of other data, we may inquire what would be the measure of the effect if the loss here had been the same in quantity as actually occurred in the experiments of Boussingault and in those by Mr. Rockwood and myself.

Taking 15 per cent. of the nitrogen of the seed as the measure of the loss in our experiments, and 45 per cent. of the nitrogen of the nitrates as the measure in Boussingault's, and assuming similar loss in the experiments here under discussion, the influence of each loss upon the main result would be as shown in the last three columns of Table IV.

While it would be absurd to claim that either of the percentages of loss above named is a correct measure of the actual loss in my experiments, and that the figures in either of the last two columns of Table IV are consequently a correct statement of the quantity of nitrogen acquired from the air in any one of these experiments, it is nevertheless clear that if we are willing to allow any such escape of nitrogen here as was actually observed in the analogous experiments of Boussingault, in which the loss was estimated, the effect upon the results would be considerable. If we were to assume, for instance, that the loss was confined to the nitrates in the concentrated solutions and was equal to that observed by Boussingault, we should have in these cases (Nos. 5, 6, 7 and 8), instead of either a small gain or a loss of nitrogen, a gain of from 27 to 57 per cent. while the gain actually observed in the dilute solutions was from 38 to 51 per cent.

TABLE IV.

Acquisition of Nitrogen from Atmosphere by Peas as Actually Observed and as Computed by Allowing for Assumed Loss from Decomposition of either Seed or Nitrates of Nutritive Solution.

Conditions of Experiments.			No. of Experiment.	Gain +, or Loss —, of Nitrogen. In per ct. of Total Nitrogen of Plants.		
				As actually observed in the experiments.	Allowing 15 per ct. of the Nitrogen of the seed to have escap'd	Allowing 45 per ct. of the Nitrogen of the Nitrates of the Nutritive Solutions to have escaped.
				Per cent.	Per cent.	Per cent.
Concentrated Solutions.	Scantily fed.	Smaller nitrogen ration	7	+ 17.2	+ 23.9	+ 34.1
		Larger " "	8	+ 1.5	+ 6.9	+ 32.7
	Well fed.	Smaller " "	5	+ 40.0	+ 43.3	+ 57.1
		Larger " "	6	— 14.0	— 10.5	+ 27.2
Dilute Solutions.	Scantily fed.	Smaller " "	11	+ 38.7	+ 43.9	+ 51.4
		Larger " "	12	+ 38.1	+ 42.1	+ 61.8
	Well fed.	Smaller " "	9	+ 50.0	+ 52.8	+ 64.3
		Larger " "	10	+ 51.1	+ 52.9	+ 73.4

BEARING OF LIBERATION OF NITROGEN UPON THE RESULTS OF OTHER EXPERIMENTS. GAIN OF NITROGEN FROM AIR.

Attention was called by Mr. Rockwood and myself to the lack of uniformity in the outcome of experiments on the escape of nitrogen from seeds and plants during germination and growth. In the experiments of Schultz, in some of those of Lawes, Gilbert and Pugh, and in some of our own, the amounts of nitrogen liberated were very large, though extremely variable; and although in other cases little or no loss was observed, yet the facts now at hand amply confirm the statement of Messrs. Lawes, Gilbert and Pugh that:—

"Taking together the results of all the experiments which have been made [by the authors] upon the decomposition of nitrogenous organic matters, they obviously point to a serious difficulty in the way of experiments made upon the question of the assimilation of free nitrogen by plants. It is not possible to conduct any such experiments without exposing nitrogenous organic matter to conditions more or less analogous to those under which the loss of nitrogen recorded [in the experiments described by the authors] took place. For although, as Boussingault has shown, there may be no loss of nitrogen during germination, yet during the entire period of the growth of a plant, certain portions of the vegetable substance may be subjected to conditions favorable to the decomposition of its nitrogenous compounds and to the evolution of free nitrogen."[1]

Once granting the liability of experiments to this source of error, and considering how entirely unable we are to definitely predict the cases when nitrogen may be liberated, or determine the amount of the loss, it is perfectly easy to see how the results of different experiments on the acquisition of atmospheric nitrogen should be as conflicting as they are.

The remarkably close agreement of duplicate results and of the amounts of nitrogen supplied and found in Boussingault's experiments with plants in confined air or in a current of washed air under glass,[2] would, perhaps, imply that these experiments, in which the nitrogen compounds of the air were excluded in order to test the more accurately the question of the assimilation of free nitrogen, were not materially affected by liberation of nitrogen. Messrs. Lawes, Gilbert and Pugh were also persuaded that there was no considerable escape of nitrogen in their experiments with plants in washed air under glass in which the same question was tested.[3] Possibly plants under such conditions may be less liable to lose their nitrogen than otherwise. But, taking the observed facts together, they seem to imply that abnormal conditions of growth — *e. g.*, insufficient or unfitting nourishment — may be especially conducive to this loss of nitrogen, just as malnutrition of higher organisms renders them less capable of resisting disease.

The early experiments of Boussingault (in 1837–38) with germinating seeds, described in the preceding article, were introductory to others in which the plants were grown for two or three months or more and then analysed. These latter experiments were conducted in the free air of a closed summer-house. The plants, with the exceptions stated in the table herewith, were grown in ignited soil and watered with distilled water. The growth, without food other than that supplied by seed, burnt soil and air, was stunted, but a number of the plants nevertheless attained a respectable size, and put forth buds and blossoms. The principal data and results are given in Table V :

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[1] Phil. Trans. 1862, **2**, 512.

[2] Ann. Chim. Phys. [3], **43**, 149–190.

[3] *Loc. cit.* 514.

TABLE V.

Experiments by Boussingault.—Plants Grown in Free Air of Closed Summer-House.

Kinds of Plants and Times of Experiments.	Quantities of Nitrogen.			Parts of Nitrogen in plants for 100 parts in seed.
	In seed (or plants) at outset.	In plants at end of experime't	Gain +, or Loss —.	
	Mgm.	Mgm.	Mgm.	
Wheat, 1837, 2 months	43	40	— 3	93
Wheat, 1837, 3 "	57	60	+ 3	105
Oats,[1] 1838,	59	53	— 6	90
Clover, 1837, 2 "	110	120	+ 10	109
Clover, 1837, 3 "	114	156	+ 42	137
Clover,[2] 1838,	33	56	+ 23	170
Peas, 1838, 3⅓ "	46	101	+ 55	220
Total : 9 experiments	462	586	+122	132

With the cereals, wheat and oats, the quantities of nitrogen supplied in the seed and found in the plant were about the same, though on the average there was a slight loss of nitrogen. The clover contained at the end of the experiment from 109 to 170 parts, and the peas 220 parts of nitrogen. The excess, barring small errors incident to manipulation, must have come from the air.

The conditions of these experiments were quite similar to those of the experiments of Mr. Rockwood and myself, already referred to, on the germination and growth of peas. The plants in both cases were grown in free air. Boussingault's[1] were in a closed greenhouse. Part of ours were in a greenhouse, part in a dwelling-house, and part out of doors, but protected from rain and dew. Both Boussingault's plants and ours were without nitrogenous food except that supplied by the seed. Boussingault's plants very likely got mineral food from the burnt soil which ours could not get from the washed and ignited sea-sand. This may, perhaps, explain the fact that his plants appear to have been much thriftier than ours. Some of his, indeed, had well-developed seeds. His clover and peas acquired considerable nitrogen from the air in every case, while our peas as uniformly lost nitrogen. It will be remembered that when, in the same series of experiments, he stopped the growth during or near the end of the period of germination, no considerable amount of nitrogen had escaped, while our peas at a nearly corresponding period of development showed a loss of nitrogen. And the gain which Boussingault observed was in accordance with the fact that in my assimilation experiments with peas, the plants receiving food in nutritive solutions and grown in open air out of doors acquired such large quantities of atmospheric nitrogen.

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[1] The plants were started in a field, then taken up June 10, three analysed, and four placed with their roots in distilled water, where they grew and flowered. August 10 they appeared ripe, and were dried and analysed.

[2] The plants were started in ordinary soil, taken up May 28, three analysed and three set out again in purified sand, where they were kept moist with distilled water, and grew, flowering in the middle of July, until August 1st, when they were dried and afterwards analysed.

In the years 1851–54 Boussingault made several series of experiments[2] with haricot beans, lupines, oats, wheat and garden cress, which were grown in ignited sand soil or pumice, fed with ashes of plants or of manure, and moistened with pure water. They were enclosed in a glass case, which was kept in open air out of doors. The case was, however, opened slightly around the bottom and top, so as to allow circulation of air from outside through the case, but to exclude rain and dew. The plants were supplied with the mineral food of the ashes, but no nitrogen except that in the seed and ambient air. The exposure to air was much more limited than if there had been no glass case. The plants were stunted in growth, but had blossoms and, in some cases, ripe seeds. Details and results are summarised in Table VI.

There is here a gain of nitrogen in every experiment but one. Even the cereals, oats and wheat, contain from 17 to 32 per cent. more than was supplied by the seed. The results differ from those of the previous series in that the cereals here show more, and the legumes less, gain of nitrogen. On the whole, there is a smaller gain of nitrogen in this than in the previous series.

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[1] Ann. Chim. Phys. [2] **67**, 5, and **69**, 353.

[2] Ann. Chim. Phys [3] **43**, 1855.

TABLE VI.

Experiments by Boussingault.—Plants Grown in Glass Case with Limited Supply of Air.

Kinds of Plants and Times and Numbers of Experiments.	Quantities of Nitrogen.			Parts of Nitrogen in plants for 100 parts in seed.
	In seed at beginning of expt.	In plants and soil at end of expt.	Gain +, or Loss —.	
	Mgm.	Mgm.	Mgm.	
Dwarf haricot, 1851, '53 and '54, 2½ to 3½ months, 3 expts.	29.3 to 34.9	27.0 to 38.0	—2.3 to +3.2	92 to 110
Haricot, 1852; 3 months, 1 expt.	21.3	23.8	+2.5	112
White lupine, 1853, 3 months, 1 expt.	21.4	25.6	+4.2	120
Lupine, 1854, 2¾ and 2 months, 2 expts.	19.9 & 36.7	22.9 & 38.7	+3.0 & +2.0	115 & 105
Oats, 1852, 3½ months, 1 expt.	3.1	4.1	+1.0	132
Wheat, 1853, 3½ months, 1 expt.	6.4	7.5	+1.1	117
Garden cress,[1] 1854, 2 months, 1 expt.	25.9	27.2	+1.3	105
Total in 10 expts.	230.7	249 9	+19.2	112

Boussingault suggests that the distilled water which was used for watering the plants of his first series, and which was directly distilled from ordinary river water,[2] may have contained traces of ammonia, which might, perhaps, account for the larger gain of nitrogen in the first series. But it is difficult to see how this could account for the fact that while, in the first series, the legumes acquired relatively large quantities of nitrogen from the air, and the cereals practically none, the cereals in the second series showed a large gain and the legumes sometimes a smaller gain, and in one case a loss.

The differences in the results of similar experiments in the two series just cited are very wide. In a research so remarkable for the care and accuracy manifested in its chemical work as to have since come to be regarded as a classic model in this respect, these discrepancies can hardly be ascribed to errors of analysis, especially when one takes the pains to examine the details of the work. Where the quantities are so small as in the experiments with wheat and oats in 1852–3, such an assumption might be allowable, but in the other cases some other explanation seems called for. A very simple explanation is found in the supposition that nitrogen was liberated in varying quantities in the different experiments.

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[1] 210 seeds were sown; 145 grew, the remaining 65 "acted as manure." That the latter may have lost nitrogen by decomposition would seem by no means improbable. If such was the case, the actual gain of atmospheric nitrogen must have been more than the figures imply.

[2] At the time of the first of Boussingault's experiments the occurrence of minute quantities of ammonia in air and water was not so well understood as it afterwards came to be through his and other researches.

To resume briefly: These experiments of Boussingault, with plants grown in open air the circulation of which was limited and with limited supplies of food, so that the growth was abnormal, gave these two very marked results:

1. Very considerable quantities of nitrogen were obtained from the air. 2. The acquisition of nitrogen, as measured by subtracting the nitrogen supplied from that found at the end of the experiment, was very irregular. Assuming that nitrogen compounds were decomposed and nitrogen set free in varying quantities in the different experiments, as was evidently the case in the numerous instances above discussed, the explanation is very clear. No other so simple and reasonable hypothesis has occurred to me.

Among the well-known experiments on the acquisition of atmospheric nitrogen by plants, are those of Mayer,[1] who has tested the absorption of atmospheric ammonia by the foliage of plants, and concludes that though this is theoretically possible, it probably is so small in extent as to have little or no practical importance.

Excellent as is this research, a careful examination of the details will, I think, warrant the conclusion that the conditions of growth were exactly those which the considerations named above imply to be favorable to the liberation of nitrogen. The plants were, for the most part, very inadequately nourished, that being one of the intended conditions, and were generally stunted and sickly. In cases in which the development was more vigorous, the nutritive solutions were, as the data imply, as concentrated as those in my experiments, in which the escape of nitrogen seems so well established. Here again, therefore, the evidence against the acquisition of nitrogen is seemingly impaired by the abnormal conditions of growth and the, at least possible, escape of nitrogen.

Dietzell concludes, from experiments with peas and clover, that these plants do not assimilate atmospheric nitrogen compounds by their foliage, but here, also, the conditions appear to have been such as to furnish no proof that nitrogen did not escape.[2]

Weiske[3] has reported a series of water-culture experiments with lupines which showed, in a number of cases, a small gain of nitrogen. The plants, however, were stunted and for the most part sickly, and even the healthiest were, in development, "far behind those grown under natural conditions." In one case the plants were cultivated, not in aqueous solution like the rest, but in fragments of filter paper contained in an evaporating dish and kept moist with the nutritive solution, the object being to provide for absorption of nitrogen compounds from the air, and for possible formation of ammonium nitrite by evaporation. In another case the cylinder containing the nutritive solutions was covered tightly, to prevent both absorption of nitrogen compounds and evaporation.

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[1] Landw. Vs. St. **17**, 329.

[2] Landw. Vs. St. **31**, 1884, 166, and Jbt. Ag. Chem. 1884, 297.

[3] Landw. Vs. St. **30**, 1884, 437.

The weight of the plants and the acquisition of nitrogen were both very small where the air was thus excluded, and somewhat larger where the full opportunity was given for access of air and for evaporation. In the last-named case, the one in which the growth of the plants was greatest, the nitrogen in the seed (there was none in the nutritive solution) was 11 mgm. and that in the plant 18 mgm., making a gain of 7 mgm. Weiske infers that nitrogen was acquired from the air, either directly as ammonia, or indirectly by formation of ammonium nitrite through evaporation, but that it came to the plants through the roots rather than the foliage. Considering the abnormal character of the plants, and the small differences between the nitrogen of the seed and that of the plants, the experiments do not seem to me decisive regarding the route through which the atmospheric nitrogen came.

Joulie[1] has lately published accounts of experiments in which there was a large acquisition of nitrogen from the air. The plants were grown in soils contained in glass pots, and kept in open air, but protected from rain and dew. The experiments were conducted through two successive years. In one series buckwheat was grown the first year and ray-grass and hybrid clover the second; in the other, there were no plants the first year and buckwheat the second. In some cases fertilizing materials were used, in others not. The nitrogen supplied and that found at the end of the experiment in plants and soil were compared. Of twenty-two cases cited, two showed a loss and the rest more or less gain of nitrogen. The gain in one case reached 865 mgm. or 577 mgm. per kilo of soil.

The results are very similar to those obtained by myself. Joulie

[1] Compt. Rend. **101**, 1885, 1008.

is inclined to ascribe the gain to the fixation of free nitrogen, perhaps by the soil through the agency of micro-organisms, in the manner indicated by Berthelot.

OTHER CONSIDERATIONS REGARDING THE SOURCES OF PLANT-NITROGEN.

The fact observed in many experiments, that nitrogenous food supplied to the roots of plants, legumes as well as cereals, causes increase of growth, and that the produce, other things being equal, rises and falls with the amount of nitrogen supplied, has been frequently interpreted as indicating that the soil is the only source of the nitrogen of the plants. The field experiments of Messrs. Lawes and Gilbert afford evidence in this direction[1] which, taken by itself, seems very cogent. In these, as the plants are grown year after year on the same land without artificial supply of nitrogen, the yield gradually falls off, and the stock of nitrogen in the soil is at the same time depleted. This is particularly the case with cereals—wheat, barley, etc.—though the same fact is observed with other plants. It is perfectly legitimate to infer that the crops have taken the nitrogen away, and that the succeeding produce is smaller because of this reduction of the supply of mineral food, and especially of nitrogen. The corollary is that the soil is the sole source of the nitrogen.

But we have a closely parallel, though, of course, far less extended, series of results in the experiments cited in Tables I and II above, as may be seen by comparing the "scantily fed" plants with the "well-fed" ones, or the averages with the "smaller" and with the "larger nitrogen rations." The best-fed plants throve best, and when either the total food-supply was diminished or the nitrogen-supply alone was reduced, the mineral food remaining the same, the yield fell off in corresponding degree, as did the amount of nitrogen acquired from the air. Indeed, the uniform parallelism between both the total food-supply and nitrogen-supply on the one hand, and both the total nitrogen in the plants and the amount acquired from the air on the other, was, to myself at least, very surprising.

The phenomenon which is uniformly accompanied by the acquisition of atmospheric nitrogen by the plants in Middletown can hardly prove its non-acquisition by those in Rothamsted. While the Rothamsted plants were taking nitrogen through their roots from the medium in which they grew, and thus reducing the supply of the latter, as was done by the plants in Middletown, may they not also, like the Middletown plants, have acquired some from the air?

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[1] Determination of the Nitrogen in Soils, London edition; and Jour. Chem. Soc. 1885, Trans. 380.

Late experiments by Messrs. Lawes, Gilbert and Warrington[1] lead them to the evidently well-founded and very important conclusion that the leguminous plants somehow favor nitrification, probably through the development of nitrifying ferments, and they are inclined to attribute the peculiar power of the legumes to supply themselves with nitrogen, in part at least, to this function of inducing nitrification of nitrogen compounds previously accumulated in the soil. It is evident, however, that this previously existing store of nitrogen cannot account for all the nitrogen which such plants may acquire, since in my experiments, in which peas were grown in washed and ignited sea-sand, no nitrogen compounds were supplied except the nitrates of the nutritive solution.

Against the acquisition of atmospheric nitrogen by the legumes, Messrs. Lawes and Gilbert cite the observation that clover and other plants of this family, after growing for a number of successive years in experimental fields at Rothamsted, have finally failed, while clover in a garden soil near by, much richer in nitrogen, has continued to do well for a long period of years. The soil in the field has become "clover-sick," a not uncommon experience in Europe, while the richer garden soil has not. In another field the land has become "bean-sick." In other experiments still other leguminous crops have failed after a time. This failure Messrs. Lawes and Gilbert attribute to the depletion of the store of soil-nitrogen, as well that of the lower strata where the clover does a large part of its feeding, as that of the upper strata, a supposition which is strengthened by the fact that the clover continues to grow in the rich garden soil, where the stock of nitrogen is larger. This failure of the clover, beans and other plants to grow continuously for a large number of years may, however, be due to some other cause—for instance, the injurious action of minute organisms, such as have been found by late researches to be a probable cause of the "beet-sickness" in Germany, where land after a time refuses to yield successive crops of sugar beets. If there are organisms which thrive upon a specific plant, as the beet, and, when the latter is continuously cultivated, increase until they materially injure it, why may not clover, beans and other plants suffer in like manner? This assumption would accord perfectly with Messrs. Lawes and Gilbert's observation, that the field which has become " bean-sick " is still competent to grow luxuriant crops of red clover, and is, at least, as easy to accept as the hypothesis suggested by Messrs. Lawes and Gilbert, that the success of the one legume after the failure of the other is due to difference of root-habit and root-range.

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[1] *Loc. cit.*

The Rothamsted field experiments with wheat and barley afford a most striking indication that no considerable quantity of nitrogen is obtained from the air by either these plants or by the soil, in the balance between the income and outgo of nitrogen. Putting on the one side of the account the total nitrogen in the soil, as shown by analysis at the beginning of a long period of years, together with the amount estimated to be brought to the soil by the measurable aqueous deposits, rain, snow, etc., during the same period, and on the other the amounts removed with the crops and with drainage water and the amounts left behind in the soil at the end, the two sides of the account balance with remarkable closeness. The accuracy of this balance implies that the account is correct, and that no other item, such as nitrogen acquired from the air, could be admitted. But this assumes that no considerable loss of nitrogen by decomposition of nitrogenous compounds, such as the facts at hand would lead us at least to regard as possible, can take place, nor does it make any allowance for the acquisition of nitrogen by the soil through the agency of electricity or of micro-organisms, the activity of both of which is indicated by late investigations of Berthelot. On the other hand Messrs. Lawes and Gilbert,[1] Dehérain,[2] Schulz-Lupitz[3] and Heiden,[4] have observed that soils on which leguminous crops had been cultivated for a longer or shorter period have contained more nitrogen than they did before. In the experiments of Lawes and Gilbert, which were with clover, only the surface soil was tested; the first nine inches showed an increase of nitrogen. In Heiden's experiments, observations were made in both surface and subsoil, and the increase of nitrogen in the subsoil during growth of clover after a dressing

[1] Am. Jour. Sci. [3] **3**, 28. [2] Ann. Agronom. 1882, 322. [3] Ct. Bt. f. Ag. Chem. 1883, 145.

[4] See von Bretfeld, Das Versuchswesen a. d. Geb. d. Pflanzenphysiologie, 176.

of lime was very marked. That is to say, while these leguminous plants were acquiring their large quantities of nitrogen, which was to be removed with the crop, the store of nitrogen in the soil was, according to these observations, not depleted, but rather increased. This extremely interesting phase of the general subject demands further study. Meanwhile it is safe to say that the acquisition of atmospheric nitrogen will explain the phenomenon, which otherwise is hardly explicable.

Many familiar facts, such as the often observed facility with which many legumes obtain their large supplies of nitrogen where cereals and other plants fail for lack of it; the thrifty growth of some of these plants in sand, where the soil supply of nitrogen is extremely limited; and the very common refusal of legumes to respond to the application of nitrogenous fertilisers, when the growth of other plants is materially helped by them, all point to a peculiar power of at least some species of plants to provide themselves with nitrogen from natural sources, and are easily understood if we allow that some of their nitrogen comes directly from the air; while, if this assumption is denied, the facts can hardly be explained.

Two different ways by which the free nitrogen of the air may be made available to plants have been suggested by late researches of Berthelot. One is the fixation of nitrogen by vegetable matters through the agency of electricity.[1] The acquisition of nitrogen by living plants through this means will doubtless be best discussed after the publication of further results which Berthelot has promised. The other is the no less remarkable observation that soils containing clay may fix large quantities of free nitrogen through the aid of living organisms,[2] which may perhaps give us an explanation of the increase of nitrogen in the soils on which leguminous plants have been grown by Lawes and Gilbert, Dehérain, Schulz-Lupitz and Heiden. I do not see how they can explain the acquisition of nitrogen in my own experiments, however. It would seem that if the fixation of nitrogen in my experiments was due to the agency of microbes, the plants themselves must have had a share in the operation, since neither purified sand alone, nor an aqueous solution of salts, nor both together, so far as I am aware, have ever been shown to have any power of

[1] Ann. Chim. Phys. **10**, 52, and **12**, 457.

[2] Compt. Rend. **101**, 775.

gathering nitrogen, except in so far as solutions may take nitrogen compounds from the air.

In brief, strong as is the evidence which comes from the greenhouse and the field in support of the view that neither the legumes nor any other plants acquire any material amount of nitrogen from the ambient air—and, leaving loss of nitrogen by decomposition out of account, this evidence is extremely cogent—it nevertheless fails to explain some of the most important of the observed facts of production, and is circumstantial and cumulative rather than positive and absolute, and hence cannot avail against absolute testimony on the other side.

The considerations above urged regarding the liberation of nitrogen seem to me to help greatly toward explaining the negative results that have been so often obtained. Positive evidence of the acquisition of atmospheric nitrogen by plants is furnished not only by my own experiments, but by those of Joulie and others in the greenhouse and laboratory, and is reinforced not only by the testimony found in the field by Lawes and Gilbert, Dehérain, Schulz-Lupitz and Heiden, but also, though with less definiteness, by the facts of common observation.

CONCLUSION.

The considerations above presented may be summarised as follows:

1. The experiments in which peas were grown in open air, as detailed in a former, and recapitulated in the beginning of this article, showed in some cases a large acquisition of nitrogen from the air, the gain amounting in some instances to half or more than half of the whole nitrogen in the plants. In other cases there was, apparently, a very small gain or a loss of nitrogen. There seems to be excellent ground for assuming that the cases in which either only a small gain or a loss of nitrogen was observed (in all of which the conditions of growth were abnormal) are to be explained by the escape of nitrogen from either the nitrates of the nutritive solution or from the seeds during germination, or from the growing plants. The proof of the acquisition of atmospheric nitrogen which is furnished by the cases in which the conditions of growth were normal, in each of which the amount acquired was large, is thus rendered the more emphatic.

2. That plants grown in open air may acquire nitrogen from the air was long ago observed by Boussingault. His plants, however, received no nitrogen except that from the seed, and the quantities of atmospheric nitrogen acquired were small. The fact that so much more was obtained in my experiments, in which the plants were liberally supplied with food, may be explained by either of two very plausible hypotheses. The plants grown under normal conditions may have been in better condition to resist the action of denitrifying ferments or other agencies which would set nitrogen free, or they may have been better able to assimilate nitrogen from the air. Of course these hypotheses need further proof before they can be entitled to unqualified acceptance. The lately published experiments of Weiske, and especially those of Joulie, afford still further corroboration of the acquisition of nitrogen from the air.

3. Numerous other experiments have shown very slight gain or more or less loss of nitrogen, so that the evidence at hand, taken altogether, is quite conflicting. The liberation of nitrogen from the germinating seeds, as well as from the nitrogenous food supplied, affords a simple and, to say the least, not unreasonable explanation of much of the discrepancy. That there is liability to such loss, at times very considerable, is certain. Tending, as it does, to reduce the quantity of nitrogen found at the end of the experiment, and hence the quantity apparently acquired from the air, it is easy to see how there might really be a considerable gain of nitrogen from the air in an experiment in which the comparison of the nitrogen supplied with that found at the end implied only a small gain or even a loss. The failure of an experiment to show the acquisition of nitrogen from the air proves the non-assimilation of atmospheric nitrogen only on condition of the further proof that no nitrogen was liberated, while a gain actually observed is positive proof that the nitrogen is assimilated either directly by the plants or indirectly through the medium in which the roots developed.

4. The liberation of nitrogen appears to be due, in some cases, if not in all, to ferments. To explain why it should take place in one case and not in another, is as difficult as to account for the fact that zymotic diseases attack one animal and not another, or that the potatoes of certain fields or some of the apples in a barrel are struck with decay, while others escape. It is, however, notice-

able that in nearly all the experiments in which no gain of nitrogen has been observed the plants have been ill fed, or the nutritive solutions have been very concentrated, or other conditions have been abnormal; while, so far as the details at hand show, the largest gains have been found in the cases where the conditions of growth were most favorable. This accords with the common observation that organisms weakened by insufficient nourishment or otherwise are generally less able than those in normal condition to resist zymotic diseases.

5. How the nitrogen was obtained in the experiments in which its acquisition is proven is still a matter of doubt. It must have been taken as either free or as combined nitrogen, and either directly through the foliage or indirectly through the soil and nutritive solutions and the roots of the plants.

6. It would be going too far to positively assume that in the experiments which have given the strongest evidence against the fixation of free nitrogen by plants—namely, those of Boussingault and of Lawes, Gilbert and Pugh, in which the plants were raised under glass, in confined air or in air washed free from nitrogen compounds—the negative results are due to escape of nitrogen in the manner above suggested, though such liberation cannot be regarded as impossible. But it is at least conceivable that the measures adopted to exclude nitrogen compounds—keeping the plants under glass and passing the air through acid and alkali solutions before entering—may have excluded the action of electricity or of microbes, by which the fixation of free nitrogen may perhaps be effected. The plants were also, for the most part, very poorly fed. That this may be the cause of deficient assimilation of nitrogen is indicated by the experiments with peas above referred to. At any rate, until we know more about the relations of electricity and of micro-organisms to the fixation of nitrogen, we can hardly be warranted in assuming that these experiments prove that plants grown under normal conditions do not assimilate the free nitrogen of the air.

The fact that the observed cases of large acquisition have been with plants in open air, might be taken as indicating that the ammonia and other nitrogen compounds of the atmosphere are the source of the nitrogen obtained, were it not that the amounts acquired have, in some cases, been several times as large as the apparently possible maximum.[1]

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[1] This Journal **6**, 376–381.

7. To what extent the attested acquisition of atmospheric nitrogen is a function of the plant alone; in how far it may be dependent upon the action of electricity, microbes, or other agency induced by the plant; by what species of plants and under what conditions it is accomplished, are of course matters for further study. The experiments of Berthelot imply that organic matter, through the agency of electricity, and soils containing clay, through the agency of living organisms, may fix the free nitrogen of the air. It may hence be inferred that in some of the experiments in which acquisition has been observed, the nitrogen may have been first taken from the air by the medium in which the roots grew and communicated through the latter to the plants. But in my experiments this medium consisted of ignited sea-sand and an aqueous solution of salts. I am aware of no observed facts to imply that these, separately or together, are able to fix free nitrogen by aid of electricity, micro-organisms, or any other means. In the present state of our knowledge, therefore, the balance of probability seems to decidedly favor the assumption that the plants themselves must be factors in the acquisition of atmospheric nitrogen.

8. Messrs. Lawes, Gilbert and Warrington have shown the great probability that the legumes, which appear to possess in high degree the power of obtaining nitrogen from natural sources, induce the action of nitrifying ferments by which the inert nitrogen of the soil is made available. It is equally conceivable that the same plants and others may favor the action of nitrogen-fixing micro-organisms.

To recapitulate in few words: The experimental testimony regarding the acquisition of atmospheric nitrogen by plants is conflicting. But the evidence against it which comes from the laboratory and the greenhouse is based upon experiments whose conditions were more or less abnormal in respect to food-supply or access of nitrogen compounds or otherwise. In those which seem most conclusive against the assimilation of free nitrogen the arrangements were such as may have hindered the action of electricity, if not that of nitrogen-fixing micro-organisms, two agencies toward which late research points as possible, if not certain, factors in the fixation of nitrogen. In all there is the possibility, and in some a very strong probability, that the results may have been affected by liberation of nitrogen from seeds or plants or food supplied, a liberation which is sometimes, if not always, due to ferments. This may materially reduce the nitrogen found at the end of the experiments, and with it the apparent gain of nitrogen from the air. The evidence from the field against the assimilation is of necessity more or less incomplete, since, to say nothing of other difficulties, some of the important factors of the problem, such as the acquisition of nitrogen by the soil and its liberation from the soil, are inadequately settled or left entirely out of account. And, finally, to deny the acquisition of atmospheric nitrogen is to leave some of the most evident facts of production unexplained.

On the other hand, the evidence in favor of the acquisition of nitrogen by plants, legumes especially, from the atmosphere during their period of growth is direct and positive. In pot experiments the gain has been at times very large, and in comparative trials it has been larger or smaller in proportion as the conditions have been more or less nearly normal. Less accurate, but at the same time very strong, evidence in the same direction comes from experiments in the field. The conclusion that plants acquire atmospheric nitrogen accords with and explains facts of vegetable production otherwise unexplained. And late research leads us to hope that the explanation of the processes by which the nitrogen is acquired may be found, perhaps, in the near future.

It is reasonably certain that the combined nitrogen of the atmosphere is assimilated by plants. If the results of research should continue to develop in the same direction in which they have been developing of late, it will require but a short time to place the assimilation of free nitrogen beyond question. Unless future research should bring evidence directly opposed to the best now at hand, it must be allowed that the greater part of the nitrogen which the plants obtain from the air comes through the foliage. The faculty of obtaining nitrogen from the air appears to be especially characteristic of the legumes. By what species of legumes or other families of plants it is possessed, it is as yet impossible to say.

But, whatever may be the plants that acquire atmospheric nitrogen, the ways by which they acquire it or the form in which it comes, the fact of its acquisition in considerable quantities seems well established.

MIDDLETOWN, CONN., *July* 1, 1886.

THE INDIRECT ESTIMATION OF CHLORINE, BROMINE AND IODINE BY THE ELECTROLYSIS OF THEIR SILVER SALTS.

WITH EXPERIMENTS ON THE CONVERTIBILITY OF THE SILVER SALTS BY THE ACTION OF ALKALINE HALOIDS.

BY J. EDWARD WHITFIELD.

In the absence of reliable methods for the direct quantitative separation of bromine and chlorine, it is usual to employ one or other of the methods for the conversion of the mixed silver salts to a common condition.

Both the reduction to silver by hydrogen and the conversion of the bromide to chloride by heating in an atmosphere of chlorine are attended with loss by volatilisation and mechanical transfer, and the possible inaccuracy of both the processes is such that they can scarcely be considered as available for the estimation of small amounts of either constituent in presence of large amounts of the other.

Of all such methods the electrolytic analysis of the mixed and fused silver salts, as proposed by Bolley,[1] and more recently introduced and tested by Kinnicutt,[2] is probably the best, though, according to Finkener,[3] perfect decomposition is difficult to obtain by this method, and there is danger of volatilisation and partial change of the silver salts in the fusion.

Kinnicutt's test analyses of the fused salts show, for silver chloride and silver bromide each by itself, errors of 0.0006 gram — to 0.0003 gram + on amounts varying from 0.7 gram to 1.8 grams; and for the mixed silver chloride and bromide, errors from 0.0010 gram — to 0.0012 gram +, with a mean of 0.0006 gram + on weights varying from 2 grams to 2.8 grams.

These figures represent the sum of the errors from the weighing of the fused chloride to the weighing of the deposit of silver, and do not include errors made in the precipitation, filtration, transfer to crucible and fusion.

A method in which the decomposition of the silver salts may be effected without fusion, and which would at the same time place the errors of filtration, preparation for weighing and subsequent electrolysis at a minimum, seems to be desirable, and a promising line of investigation was suggested by Luckow's assertion[1] that from the solution of silver chloride in potassium cyanide the silver may be thrown down completely.

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[1] Dingl. Pol. Jour. **151**, 46. [2] This Journal **4**, 22. [3] Rose-Finkener, Quant. Anal. **2**, 621.

Luckow gives no figures excepting a common mean of all determinations by the precipitation from the cyanide solution and the decomposition of the solid chloride on the negative pole of the battery under sulphuric acid, so that the first experiments were made to test the accuracy of the battery process under these conditions.

In experiments (1)–(5) silver chloride was the starting-point. In (1)–(3) the freshly precipitated and carefully washed chloride was dried to a constant weight in a platinum dish, protected from the light, at a temperature of about 150° C., dissolved in potassium cyanide, and electrolysed after the addition of a little sodic hydrate, preliminary analyses having seemed to indicate that the presence of sodic hydrate affected the deposition favorably. In all subsequent experiments ammonia, which was found to be of equal service, was used instead of sodic hydrate.

In experiments (4) and (5) the chloride was converted, previous to electrolysis, into the bromide by solution in potassium cyanide, the addition of potassium bromide and precipitation by sulphuric acid as will be described later, and the precipitate redissolved in potassium cyanide, the object being to test the action of the battery upon the cyanide solution of the silver bromide.

	AgCl taken.	Silver found.	Silver calculated.	Error.	
(1)	0.1565 gram.	0.1177 gram.	0.1178 gram.	0.0001 gram	—
(2)	1.3004	0.9785	0.9787	0.0002	—
(3)	2.2657	1.7047	1.7051	0.0004	—
(4)	0.7472	0.5618	0.5624	0.0006	—
(5)	0.2854	0.2133	0.2147	0.0014	—

These results, as far as they go, are satisfactory. Similar tests upon the electrolysis of silver bromide and silver iodide in the cyanide solution were undertaken, but it was thought advisable to combine, incidentally with the tests of the battery process, an examination of the method recently proposed by Maxwell-Lyte[2] for the direct conversion of silver chloride to the bromide and thence to the iodide.

Field[3] was the first to propose a quantitative conversion of silver chloride to the bromide by digesting the former in potassium bromide, and the change of the chloride or bromide to the iodide by the action of potassium iodide upon these salts. This method has been variously criticised and finally abandoned as an accurate process,[1] though, so far as concerns the conversion of the chloride and bromide to the iodide, Siewert[2] shows it to be exact.

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[1] Dingl. Pol, Jour. **178**, 43.

[2] Chem. News **49**, 3.

[3] Jour. Chem. Soc. 10, 234.

Maxwell-Lyte's method of proceeding, depending upon identically the same principle which Field attempts to utilise, consists in the solution of the silver haloid salts in potassium cyanide, the addition of potassium bromide, the decomposition of the potassium cyanide by means of sulphuric acid, with the consequent precipitation, and weighing of the silver bromide mixed with the iodide of the original mixture—the resolution of this precipitate in potassium cyanide, the addition of potassium iodide, the decomposition of the cyanide as before, with sulphuric acid, with the formation of a precipitate which is presumably pure silver iodide and to be weighed as such.

To convert the chloride to the bromide Maxwell-Lyte uses a weight of potassium bromide equal to the weight of the silver chloride taken; and to change the bromide to the iodide, a weight of potassium iodide one and a quarter times as great as the original weight of the silver chloride.

In the following experiments these amounts have varied widely, but the proportions of alkaline haloid salts employed are given for each case in the tabular statement.

The starting-point was generally freshly precipitated silver chloride, but in the last three cases, pure silver, this being dissolved in nitric acid, precipitated with potassium bromide (two equivalents), and the precipitate dissolved in potassium cyanide, converted into the iodide in the manner described, and weighed, the object of this being to test the convertibility of the silver bromide to silver iodide.

In most cases the final precipitate, after weighing, was electrolysed, so as to have a more perfect control upon the results of the conversion process, and at the same time to test the battery method additionally.

The bromide and iodide of silver were precipitated hot from dilute solutions, which were cooled and allowed to stand over night to settle before filtering.

Filtrations were made by the use of the Gooch crucible, with gentle pressure; the silver salts were dried directly over a low Bunsen flame at a temperature far below the melting-point, and dissolved, after weighing, by introducing crucible and asbestos into a strong solution of potassium cyanide, and heating, the time necessary for the solution varying from a few minutes to several hours, according to circumstances.

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[1] Rose-Finkener, *loc. cit.*

[2] Zeit. für anal. Chem **7**, 469.

In some cases traces of reduced silver were found with the asbestos, and were recovered by treating the felt with nitric acid and washing, the filtrate and washings being added to the main solution.

The deposition of silver was made in the platinum dish of 100 $cm.^3$ capacity, which held the solution, and the current found most suitable was (as Luckow originally recommended[1]) developed by four Meidinger cells of large size.

With solutions of the volume named and the area of the negative electrode employed, it was found advisable not to attempt to treat more than two grams of the silver salt.

The solution was decanted immediately on the stopping of the current, or better, syphoned off while the battery connections were still unbroken, and washed with distilled water, to prevent the solvent action of the cyanide on the deposit.

	AgCl taken.	AgBr found.	AgBr calculated.	Error.	Equivalents of KBr taken.
(6)	0.3260 gram.	0.4227 gram.	0.4270 gram.	0.0043 gram —	2
(7)	0.3093	0.4023	0.4052	0.0029 —	2
(8)	1.3801	1.8041	1.8080	0.0039 —	2
(9)	0.2091	0.2723	0.2739	0.0016 —	10
(10)	0.6846	0.8909	0.8968	0.0059 —	10
(11)	1.1625	1.5202	1.5230	0.0028 —	20
(12)	1.1734	1.5310	1.5372	0.0062 —	20
(13)	0.3501	0.4553	0.4586	0.0033 —	29
(14)	0.4178	0.5468	0.5473	0.0005 —	29

	AgCl taken.	Silver found.	Silver calculated.	Error.
(6)	0.3260 gram.	0.2443 gram.	0.2453 gram.	0.0010 gram —
(7)	0.3093	......	......	......
(8)	1.3801	1.0385	1.0386	0.0001 —
(9)	0.2091	......	......	......
(10)	0.6846	0.5137	0.5152	0.0015 —
(11)	1.1625	......	......	......
(12)	1.1734	0.8829	0.8831	0.0002 —
(13)	0.3501	0.2634	0.2634	0.0000
(14)	0.4178	......	......	......

[1] *Loc. cit.*

	AgCl taken.	AgI found.	AgI calculated.	Error.	Equivalents taken of KI.
(15)	0.6996 gram.	1.1451 gram.	1.1456 gram.	0.0005 gram —	2
(16)	0.7587	1.2429	1.2424	0.0005 +	2
(17)	0.6710	1.0992	1.0988	0.0004 +	10
(18)	0.2515	0.4118	0.4118	0.0000	10
(19)	0.6501	1.0646	1.0646	0.0000	10

	AgCl taken.	Silver found.	Silver calculated.	Error.
(15)	0.6996 gram.	0.5255 gram.	0.5265 gram.	0.0010 gram —
(16)	0.7587	0.5691	0.5710	0.0019 —
(17)	0.6710	0.5042	0.5050	0.0008 —
(18)	0.2515	0.1892	0.1892	0.0000
(19)	0.6501	0.4892	0.4892	0.0000

	Silver taken. gram.	AgI found. gram.	AgI calculated. gram.	Error. gram.	Equivalents taken of KI.	Silver found. gram.	Error. gram.
(20)	0.5418	1.1790	1.1789	0.0001 +	2	0.5417	0.0001 —
(21)	0.3750	0.8154	0.8159	0.0005 —	2	0.3746	0.0004 —
(22)	0.4078	0.8859	0.8873	0.0012 —	10	0.4077	0.0001 —

From these experiments it appears that the deposition of silver from the cyanide solution of the chloride, bromide or iodide is exceptionally exact; the tendency of the process, however, is to yield low results, and yet, in spite of the multiplicity of operations through which the original material has been passed in the attempt to settle two questions at once, the deficiency is not very great, being 0.0005 gram in the mean of eighteen determinations, with a maximum value of 0.0019 gram.

The conversion of silver chloride to silver bromide by the method proposed by Maxwell-Lyte is, like its predecessor, too imperfect to be worthy of trust; but the experiments indicate unmistakably that the change of silver chloride or silver bromide to silver iodide is sufficiently complete to afford the basis of a good analytical method.

The indirect estimation of chlorine and bromine, chlorine and iodine, or bromine and iodine, in presence of one another, may be effected satisfactorily, therefore, by precipitating both together as silver salts, filtering on asbestos, washing, drying at 150° C., weighing, dissolving the residue in potassium cyanide, and either electrolysing the solution to determine the silver or precipitating the silver as iodide, again filtering upon asbestos, washing, drying and weighing.

In a mixture of all these halogens the iodine is first to be separated by known methods and the chlorine and bromine indirectly estimated as described.

LABORATORY OF U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C., *June*, 1886.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XV.

Communicated by F. P. Dunnington.

127.—ON MERCUROUS HYDRATE.

By G. B. Bird.

Since cupric hydrate is readily formed by precipitation, at common temperatures, with an alkaline hydrate, and is subsequently so easily decomposed by heat, it appeared probable that, while the oxides of silver and mercury are precipitated from their solutions by alkaline hydrates, the corresponding hydrates of these would be formed if operating at a lower temperature. Pursuing this suggestion, in this laboratory, in 1884, Mr. J. D. Bruce undertook the formation of argentic hydrate; and it appeared that in dilute alcohol argentic hydrate decomposes at all temperatures above — 40° C.[1] Employing a similar method, Mr. Bird has endeavored to obtain mercurous hydrate.

A dilute solution of mercurous nitrate was mixed with alcohol, cooled to — 18° C., and the small amount of salt which separated filtered off, thus obtaining 70 per cent. alcohol saturated with mercurous nitrate. A similar solution of potassium hydrate was made, and in the following experiments these were used in such amounts as gave a slight excess of the potassium hydrate solution.

When mixed at common temperature these alcoholic solutions afforded the same brownish-black precipitate of mercurous oxide that is obtained from aqueous solutions. Corresponding portions of these solutions were put into test tubes and these cooled to — 37° C. and then united and mixed by stirring; a flocculent precipitate of red-amber color was slowly formed, which subsided very slowly; as this was warmed, it gradually darkened, until at — 18° C. it was of a slate-gray color, with a yellowish-green portion suspended in the liquid.

Another experiment, beginning at a temperature of — 39° C., afforded the same results.

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[1] Chemical News, No. 1301, 208.

The most satisfactory experiment was made on a morning when the temperature of the atmosphere was — 18° C.

The bottom of a test tube was perforated and the tube was then drawn out, forming a pipette, the bulb of which was at its lower end, and fitted into another test tube, in which the potassium hydrate solution was put; by this arrangement the solution could be cooled in the pipette and transferred to the tube containing the mercurous nitrate with very little alteration of temperature. Using sufficient of one solution to correspond to one pipetteful of the other, these were cooled to —42° C. The perfectly clear though somewhat viscous liquids were then mixed. At first the solution showed only a pale yellow color; after a minute a very pale amber flocculent precipitate formed slowly and remained suspended in the liquid; after two hours the temperature had risen to — 23°C., the main portion of the precipitate had subsided and was darkened a little, the suspended portion being yellowish-green; after four hours the temperature was — 18° C. and the precipitate of a dirty yellow color; after six hours the temperature was — 10° C., the color was slightly darker and more greenish. A portion of this precipitate was collected, dissolved in cold nitric acid, and proved to contain much mercuric salt.

Judging from the colors of the corresponding compounds of lead, copper, silver and mercury, it appears very probable that the pale-amber-colored precipitate obtained was mercurous hydrate, and that it readily decomposes by heat, forming, in part, mercurous oxide and water, and more largely, mercuric oxide, mercury and water.

128.—EXAMINATION OF A SUPPOSED METALLIC METEORITE FROM HIGHLAND COUNTY, VIRGINIA.

By F. P. Miles.

This specimen was received from J. K. Campbell, Esq., of Monterey, Va. It weighs about 1.5 kilograms, and is approximately a flattened oval mass of which the greatest dimensions, taken at right angles, are 15 × 10 × 3 cm., and thinning toward the edges. Upon one edge there is firmly imbedded a small piece of white sandstone, and the compact mass of iron is covered with a thin film of rust. The sp. gr. of the mass = 6 34. An analysis of a bright, clean piece of the metal gave—

Iron, ...	99.716
Phosphorus, ...	.106
Carbon, ...	.032
Sulphur, ...	.058
	99.912

Nickel and cobalt were carefully tested for, but were not present. It appears quite certain that this specimen is of terrestrial and artificial origin, and was probably produced in one of the early "bloomery" fires, from the fossil ores lying in the Clinton beds, which are largely exposed in that neighborhood; although there is no record or tradition of any such furnace in this portion of the county.

129.—ON THE FORMATION OF PLATINUM SILICIDE.

By F. P. Miles.

In an article from this laboratory, communicated by Professor W. G. Brown,[1] there is given an account of a formation of platinum silicide. A platinum crucible containing powdered topaz was placed within a graphite crucible, between these a layer of Jennings' calcined magnesia[2] was packed, and the top of the crucible luted on with clay. After heating the crucible thus charged, the platinum silicide was found within. I then proposed to search for the essential conditions of this result, and Mr. Miles has carried out the following experiments:

A supply of carbon monoxide was collected in a gas-holder and dried by sulphuric acid as used. This was passed to the bottom of a glass flask in which silicon fluoride (with some hydrofluoric acid) was generated, and thence through a glass tube which terminated in a platinum tube, made by rolling up a piece of foil and fusing the end of the glass tube to it.

The following results shed some light upon the point in question:

The flame from a hot-blast burner fed with oxygen was directed

[1] This Journal, 7, 172.

[2] Containing a trace of Na_2SO_4.

upon the platinum tube; the latter was soon perforated, the edges of the hole being well rounded and malleable. In the subsequent experiments, air was substituted for oxygen, and the hottest flame then attainable was insufficent to fuse the empty metal tube.

The silicon fluoride alone, and with carbon monoxide, was passed through the heated tube, but the metal was unaltered.

Then a little Jennings' magnesia was put inside the tube and each of these gases passed through the heated tube, with the same result. Finally the mixture of silicon fluoride and carbon monoxide was passed over the magnesia and heated, with the following results: At a bright red heat the platinum was perforated and the edge of the metal was thickened on the side next to the magnesia, forming a small amount of a mass which resembled, as far as it could be examined, the platinum silicide above referred to. It was crystalline, brittle, hardness about 4.5, fusible on charcoal before the blowpipe, and when treated with aqua regia dissolved slowly, with separation of small particles of silica.

It appears, therefore, that at the temperature employed, the decomposition of the silicon fluoride is dependent upon the presence of both the reducing gas carbon monoxide and the strongly basic element magnesium to combine with the fluorine, in order that the platinum silicide shall be formed.

130.—ANALYSIS OF A COPPER SLAG OF BRIGHT RED COLOR.

By N. A. Berry.

This slag was obtained from the Canton Copper Works, Baltimore, Md., where it is occasionally produced in the process of refining copper.

It is very tenacious and hard, breaks with conchoidal fracture and knife-like, splintery edges, having scattered throughout its mass small spherical cavities and also very minute metallic beads; is opaque, and its color varies from bright to darker scarlet. Sp. gr. $= 2.987$; H $=$ nearly 6. When reduced to powder and treated with hydrochloric and nitric acids there remained, together with silica, a pale yellow powder; this portion was fused with soda and analysed separately. The following was found present:

Soluble in acids:		Molec. ratio.
Copper,	2.50	
Cuprous oxide,	27.05	18.95
Ferrous oxide,	.25	.34
Alumina,	.43	.42
Insoluble in acids:		
Cuprous oxide,	8.64	6.05
Ferrous oxide,	11.69	16.24
Silica,	49.24	82.07
	99.80	

From the oxygen ratio for bases and silica, 1:4, it appears that cuprous oxide can combine with a surplus of silica as do the alkalies in petalite or orthoclase.[1] It is also of interest to note the *pale yellow* color of the insoluble silicate, which contains so large a per cent. of iron and copper, probably presenting the effect of mixture of the complementary colors, green and red, which would belong respectively to the simple ferrous and cuprous silicates. No doubt this slag is familiar to all copper smelters; but, since I have not been able to find it mentioned in any treatise on metallurgy, its composition may prove of interest.

131.—COMPOSITION OF MIRROR AMALGAM.

By Gessner Harrison.

In Watts's Dictionary of Chemistry[2] we find described tin amalgams having the formulæ Hg_2Sn, $HgSn$, Hg_2Sn_3, but there is no mention of the composition of the very familiar amalgam employed in making mirrors, nor do I find such in other chemical works.

A specimen of "first-class German" mirror was taken, the amalgam, well cleansed with alcohol and water, was removed and dried over sulphuric acid; its analysis afforded the following:

		Atomic ratio.
Tin, ...	83.78	8.55
Mercury, ...	16.60	1.

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[1] Amer. J. Sc. **44**, 398, 1867.

[2] **3**, 890.

Giving approximately the formula Hg_2Sn_{17}, since in the manufacture of mirrors the excess of mercury is removed from the amalgam uniformly by pressure, it follows that there will be some little variation in the amount of mercury remaining. In view of the definite compounds which may be obtained containing a larger proportion of mercury, this presents an illustration of the decomposition of a compound by pressure.

132.—ANALYSIS OF "PURE ZINC" MADE BY THE BERTHA ZINC COMPANY, PULASKI COUNTY, VA.

By G. B. Bird.

The above-mentioned company manufactures from ore, essentially calamine, an excellent grade of zinc, which afforded on analysis (by F. P. D. in 1881) the following:

Lead,	.0500
Silicon,	.0168
Iron,	.0140
Carbon,	.0580
Arsenic,	.0001
Sulphur,	...
Zinc, by diff.,	99.8611

Through the kindness of Mr. Thos. Jones, Superintendent, a portion of the commercial spelter was charged into one of the upper retorts of the furnace and redistilled at a less heat. Analysis of which gave:

Lead,	.0225
Silicon,	.0019
Iron,	.0121
Carbon,	none
Arsenic,	none
Sulphur,	.0006
Zinc, by diff.,	99.9629

It therefore appears that while other impurities are largely removed, the small amount of iron is scarcely diminished by redistillation from a fire-clay retort with iron front, such as is usually employed in the Belgian process. This metal answers excellently for most of the laboratory processes in which zinc of high degree of purity is demanded.

133.—ANALYSIS OF SHOT.

By H. Hardaway.

Seeing that the statements made as to the amount of arsenic in the lead employed for making shot are not very definite, and are apparently not based upon any recent analyses, it appeared of interest to ascertain whether or not there is so much variation in the composition of this alloy as now made. From the brands in our market the following were selected, all being clean, well-shaped bird-shot:

No. 1.—Wythe Lead and Zinc Mine Co., Virginia.
No. 2.—Merchants' Shot Tower, Baltimore.
No. 3.—Leroy Shot and Lead Manufacturing Co., New York.
No. 4.—Fatham Bros., New York.

A complete analysis of each of these was made, employing for each over 100 grams, from which the lead was separated as sulphate, but estimated by difference, affording the following results:

	No. 1.	No. 2.	No. 3.	No. 4.
Arsenic, . . .	.0824	.0393	.2725	.1413
Iron, . . .	.0986	.0167	.0099	.0121
Copper, . . .	.0072	trace	.0081	.0107
Silicon, . . .	.0041	.0050	.0002	.0023
Carbon, . . .	.0115	.0269	.0041	.0055
Lead, . . .	99.7962	99.9121	99.7052	99.8281

We find in Muspratt's *Chemistry*,[1] as to the amount of arsenic present: "The limits are from 3 to 8 or 10 parts in 1000, the lesser quantity being employed, as the lead is more ductile and the larger when it is hard." In this selection of American shot it is seen that the amount is much smaller, and the range yet wider, being from .4 to 3.0 parts in 1000. It does not appear from these results that there is any special connection between the amount of arsenic and copper and iron, yet it is to be noted that the amount of arsenic increases as that of silicon diminishes.

University of Virginia, *Sept.*, 1886.

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[1] 2, 474.

PEPSIN *VS.* ANIMAL DIGESTION.

By E. F. Ladd.

In a previous number of this Journal[1] I gave the result of trials in the artificial digestion of the albuminoids of our feeding-stuffs; in this I propose to give data showing the reliability of the method, and the close correspondence of results to those of the German trials for similar feeds, and to the few experiments made by American investigators in animal digestion.

From Kuhn's[2] tables of digestibility I give the column of averages for all substances similar to those of my own trials. While his are, in many cases, the average for several trials showing a wide range of digestibility, my own, only trials in duplicate of a single sample. Had I made more determinations, using different samples, no doubt the differences between our coefficients would be even less than they now are.

Per Cent. Albuminoids Digested.

	Pepsin method.	Kuhn's German tables.
Red clover, ...	65	67
Clover hay, ...	74	70
Lucerne, ...	78	77
Sorghum, ...	58	56
Wheat straw, ...	25	26
Pea meal, ...	88	88
Oat meal, ...	82	87
Bean meal, ...	95	90
Cotton-seed meal, ...	89	87
Wheat bran, ...	83	88
Wheat bran, ...	70	70
Linseed meal, ...	89	87
Corn meal, ...	72	78 to 85
Average for the above, . . .	74.46	74.69

So far as results obtained on similar feeds can test the reliability of a method, the proof given in the above tabulated parallels is sufficient to show the method to be worthy of further consideration. I also had a chance to make a trial with a small sample from the same material used in two of the digestion experiments at the New York Experiment Station.[1] A small sample of the *Soja hispida* bean fodder, also of the corn fodder used in these experiments, that had been taken for analysis, remained on hand when I began my experiments in pepsin digestion. These I tested, with results as follows below:

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[1] 8, No. I.

[2] Armsby's Manual of Cattle Feeding.

	Corn fodder.	Soja fodder.
Pepsin digestion, . . .	54	75
Animal digestion, . . .	49	70

Had I made trials with samples taken each day of the digestion experiment, or a single trial of all the samples mixed, the small difference between the digestion coefficients for the animal and pepsin method might have been even less. I say small difference, for small it is as determined in nitrogen, the five per cent. difference in the soja fodder representing but one-tenth of one per cent. of nitrogen; according to Armsby,[2] but little more than the probable error for a single determination in fodder analysis for the nitrogen, and less than the probable error in animal digestion.

Assuming that the animals used in the above-named experiments were of normal digestive powers, and granting that the assumed digestibility from the German tables of the grain fed was really the actual digestibility, and omitting for the time the probable influence on digestion of compounded rations, we still have a close approximation of results.

In the light of evidence obtained since that date, there seems good reason for doubting the applicability of the digestion coefficient for the corn meal in this particular instance, as assumed from the German tables. My own experiments show that with our flint corns the digestion coefficient is considerably less than that given in the German tables. The few trials made with dent or soft corns lead me to think their albuminoids have a higher digestion coefficient than the flints. It may be that the German experiments were made with dent corn, thus reconciling the difference. If this be true, then there would be little or no difference in the results between the animal and pepsin digestion in the above trials.

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[1] Third Annual Report for 1884.

[2] Wis. Exp. Station Report, 1886, 137.

I give further, for comparison, single trials made by different investigators in comparison with my own—a sample of cotton-seed meal by Armsby;[1] also four hays by Wolf.[2]

	Pepsin digestion.	Animal digestion.
Cotton-seed meal, ...	88	89
Lucerne, ...	74	75
Red clover, ...	65	60
Red clover, ...	65	57
Meadow hay, ...	57	58

Armsby[3] and others have pointed out that the relative quantity of the several nutrients in a fodder has an influence on the digestibility. "Thus, if a fodder be made over rich in starch, the digestibility of the albuminoids is decreased." This we find to be the case in artificial digestion.

	Per cent. digested.
Corn meal, ...	70
Corn meal and starch, ...	67
Corn meal and sugar, ...	54

To further test this, several trials were made with egg albumen, which when digested by itself was wholly digested; but the addition of starch or sugar diminished its digestibility, while the two added and a little corn oil, making its composition more nearly like a natural feed, reduced very much the digestibility of the albumen.

Experimenters have assumed that in a compounded ration the results are the same as with each separate component of the ration. Considerable evidence may be brought forward to show the liability of error in making this assumption. Let us note the experiments of Malfatti[4] made upon himself with maize flour, and then with maize flour and butter, and again with maize flour and cheese. The per cent. of the different parts remaining in the faeces are given—

	Maize flour.	Maize flour and butter.	Maize flour and cheese.
Dry substance, . . .	6.30	7.96	4.20
Nitrogen, ...	18.28	31.54	7.31
Fat, ...	42.14	56.03	9.34
Carbohydrates, . . .	3.42	3.69	2.32

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[1] Annual Report Wisconsin Experiment Station, 1885.

[2] Bied. Centr. 1881, 751–755.

[3] Armsby's Manual of Cattle Feeding, 244.

[4] Bied. Centr. **15**, 40–41.

We may further draw from our experiments in artificial digestion[1] of the albuminoids of fodders, in corroboration of the same—

	Per cent. in ration digested (calculated).	Per cent. digested separately.
Ensilage, ...	73.56	61.35
Corn meal, ...	89.87	86.15
Wheat bran, . . .	83.06	83.26

When a method shall have been perfected whereby the digestibility of the other constituents of a fodder may be determined, a much more correct knowledge of the real nutritive value of our feeding-stuffs may be had; and I think chemists will soon find a means of measuring the other digestible portions. Then we shall be able to determine the nutritive value of a fodder in the laboratory, where we can have the whole process under control, eliminating the almost uncontrollable influences—the individuality of the animal, nervous influences, environments, temperature, and the necessary compounding of a ration—which in animal digestion enter in to vitiate the results.

GENEVA, N. Y., *August* 17, 1886.

ON THE SOLUBILITY OF MANGANESE SULPHIDE IN MELTING POTASSIUM SULPHIDE.

BY EDO CLAASSEN.

When experimenting with vanadiferous magnetite for the purpose of determining the best way to extract from it all vanadium, the pulverised ore was oxidised and brought into a very finely divided state by a process to be described later in a paper on the extraction of vanadium. This powder was mixed with six times its weight of equal parts of sulphur and potassium carbonate, then melted in a well-covered porcelain crucible until almost all free sulphur was gone, *i. e.* until hardly a flame of burning sulphur could be seen outside of the vessel. When cold, the crucible and contents were lixiviated with hot water, the filtrate acidulated with nitric acid in a beaker, mixed, after having been heated for some time, with an excess of potassium carbonate, heated again and brought to perfect dryness in a porcelain dish. This remnant, amounting to more than four times the weight of the magnetite, gave, when melted in a crucible, a dark bluish-green mass, which, after treatment with water, furnished a red solution and a brownish deposit.

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[1] Fourth Annual Report N. Y. Experiment Station, 316.

The dark bluish-green color of the mass was evidently due to the presence in it of potassium manganate, which, as is well known, is decomposed by being dissolved in water, thereby giving a solution of permanganate and a precipitate of hydrated manganese peroxide. By the intensity of the color it was furthermore plainly proved that the amount of manganese present was not inconsiderable.

ON THE EXTRACTION OF VANADIUM AND CHROMIUM FROM IRON ORES, PARTICULARLY FROM MAGNETITE.

By Edo Claassen.

In all treatises on the extraction of vanadium from iron ores, which have come into my hands, it is recommended to use the ore for the melting process with sulphur and soda, or with saltpetre and soda, in a very finely pulverised and bolted state; in a few places a repetition of the melting is spoken of as a sure means of getting out all the vanadium present in the ore. The result may be satisfactory if iron ores, such as limonite, which are easily converted into impalpable powders, are used. In cases, however, where ores of considerable hardness, like magnetite, are to be extracted and analysed, the pulverisation alone will not, as many experiments made by me have proved, bring the substance to be operated upon into such a form and condition that, after melting, even if the work is repeated several times, the whole of the vanadium present can with certainty be expected to be transformed into a combination soluble in water.

The chief object, therefore, of my experiments described below was to find out in cases where hard ores, for instance magnetite, are to be dealt with, a short and simple way to bring these into the condition of the finest powders. Mechanical power proved to be insufficient for this purpose, as samples of magnetite brought into a very fine powder were, after ignition with soda and saltpetre, as also with soda and sulphur, and extraction with hot water, still partly magnetic, and, as was shown by special tests, they still contained some vanadium. The following method was finally resorted to, and it gave the desired result in a perfectly satisfactory way: A quantity of very finely pulverised magnetite was mixed in a capacious dish with an equal weight of water, and then with double its weight of sulphuric acid of 1.840 specific gravity; the contents of the dish became quite hot, and hence it was thought advisable to cover the vessel, so that any loss of substance might be avoided. When the reaction had ceased, the mixture in the dish was found to be in a nearly dry state. It was now transferred into a platinum crucible and heated, at first slowly, then after a time with a considerable increase of heat, until the water, then the sulphuric anhydride, and at last the sulphur dioxide formed, were entirely gone. The residue in the crucible, now probably being the oxidised ore, formed an impalpable powder of a red color, and of the greatest fineness. As will be shown below, it was in exactly the state of division wanted. I separated it into two parts and treated them as follows:

I. *Treatment with Soda and Sulphur, etc.*—One portion of the powder was mixed with six times its weight of equal parts of soda and sulphur, then brought into a porcelain crucible, which was now well covered and exposed to gradually increasing heat, until most of the free sulphur was volatilised, *i. e.* until a flame of burning sulphur was no longer visible outside the crucible. When nearly cold the contents of the crucible were thoroughly extracted with hot water, then filtered and the filtrate acidulated with dilute nitric acid, carefully avoiding loss in consequence of the escape of gas, and then set aside for some time. The liquid was now separated by means of a filter, the precipitate on it washed several times with water, and then brought to perfect dryness. By treating the dry precipitate with carbon disulphide, the free sulphur was easily removed, leaving the vanadium sulphide as a chocolate-brown powder. This, together with the filter, was incinerated in a porcelain crucible, the residue from the evaporated filtrate obtained above, in which there is always a small amount of vanadium present, added to it, and also a small quantity of soda, and the whole ignited. The melted mass, poured on a fragment of porcelain, showed, after cooling, a dark bluish-green color *caused by some sodium manganate present.* It was extracted with hot water, the filtered liquid, contained in a flask, mixed with a good deal of ammonium nitrate and boiled, until the smell of ammonia had nearly disappeared. If, after another addition of a little ammonium nitrate, a smell of ammonia is again produced, some more should be added, and the boiling, as well as the addition of a new portion of this salt, should be continued until no smell is evolved after again operating in the same way. Not a trace of the vanadic acid is reduced in this way, which is often the case when neutralising is effected by dilute nitric acid, thus causing the escape of a certain amount of vanadium. However, instead of adding ammonium nitrate, it may be allowed, in cases where a small loss of vanadium is not objected to, to make use of the old method just mentioned of neutralising the alkaline liquid by dilute nitric acid, provided the mixing is done with great care, with constant stirring, always keeping in mind that the reaction of the liquid should never, not even partly or for a moment, turn acid, but always remain at the end a little alkaline.

The liquid, thus treated with ammonium nitrate, was filtered, precipitated with neutral lead acetate (or nitrate), the precipitate washed with water, put together with the filter into a flask, mixed with a sufficient quantity of chlorhydric acid and alcohol, and digested for some time. The precipitate formed by this operation was separated from the green liquid, the filter washed with alcohol, the alcoholic liquids united, evaporated or distilled in a beaker or flask, the remnant mixed with water, treated with hydrogen sulphide, filtered, concentrated by evaporation, poured into a wide porcelain crucible, evaporated on the water bath, perfectly dried, and ignited. The remaining vanadium pentoxide, which is mostly impure, and generally contains a little vanadium oxide, gave, repeatedly moistened with a solution of ammonium nitrate and ignited and then extracted for purification with an ammonium carbonate solution or with ammonia, a liquid which, when filtered, evaporated and ignited again in a weighed crucible, left the exact amount of all the vanadium pentoxide present.

The residue on the filter left after the lixiviation of the melted mass obtained by the treatment with soda and sulphur was subjected once more to the same melting process and to all the subsequent operations, for the purpose of showing that all of the vanadium was extracted by *but one* process. The result was a good one, as only a trace of vanadium pentoxide was obtained. The residue left the second time on the filter after melting and lixiviation was then treated as follows: It was dried, extracted with carbon disulphide and digested with concentrated chlorhydric acid, which dissolved but a little of it, giving a solution not containing any vanadium or chromium. Most of the residue left here was then by digestion with concentrated nitric acid brought into solution, in which hardly more than a trace of vanadium and no trace of chromium were ascertained. It may be stated here that by the operations just described all the chromium of the ore was left undissolved; all of it was therefore evidently to be looked for in the small balance of the ore now left after treatment in the above manner. This balance was melted after drying for the extraction of the chromium and also of the vanadium, which had perhaps escaped the solvents, with six times its weight of equal parts of soda and saltpetre, the melted mass lixiviated with hot water and treated as described below under II. While all the chromium of the ore could be stated to be present in this solution, only traces of vanadium could be found in it. I think the above experiments prove clearly that by Treatment I all the vanadium of the ore finds its way into the solution, while all the chromium is left undissolved. This method of extracting and separating the vanadium is therefore highly to be recommended, particularly if the estimation of this element only is the point aimed at. If, however, it is the object of the analysis to determine the quantity of the chromium as well as that of the vanadium, it may be equally or even more advantageous to make use of the mode of extraction described below under II, which affords nearly as good results, as regards the separation of vanadium, as I.

II. *Treatment with Soda and Saltpetre, etc.*—The other portion of the ore, treated with concentrated sulphuric acid, etc. (see above), was mixed with six times its weight of equal parts of soda and saltpetre, ignited, and perfectly extracted with hot water. The residue was subjected once more to the same operation, and it was only the solution of this last melted mass that was used for the detection and estimation of any vanadium and chromium still left in it. For this purpose it was heated with such an amount of ammonium nitrate that, when the smell of ammonia had disappeared, the addition of a new portion of that salt did not produce it again. The liquid was now precipitated by neutral lead acetate, the precipitate collected on a filter, washed thoroughly, and while still moist digested with chlorhydric acid and alcohol; the filtrate evaporated to remove, besides the alcohol, most of the acid; then, after dilution with water, treated with hydrogen sulphide, filtered, evaporated and ignited. The residue, containing all the vanadium and chromium brought into solution by the last melting process, was mixed, for the purpose of separating these two elements, with soda and sulphur in the proportion of 1 : 3 : 3, and ignited until almost all free sulphur was gone. When cold, the crucible with its contents was put into boiling water; after filtering, all the chromium present was found on the filter, and all the vanadium in the solution. The filter was incinerated, and the residue mixed with six times its weight of equal parts of soda and saltpetre. After melting, the mass was dissolved in hot water, the solution filtered and precipitated as usual in form of lead chromate.

The vanadiferous filtrate, however, was acidulated in a beaker with diluted nitric acid and filtered after some time; the residue on the filter, after drying, was extracted with carbon disulphide, mixed with the evaporated filtrate before obtained, and melted. The melted mass, poured on a piece of porcelain, was dissolved in hot water, filtered, boiled for some time, after addition of ammonium chloride, then filtered again and evaporated so far that, after cooling and stirring for a while, no separation of crystals had taken place. Into this solution a lump of ammonium chloride was deposited large enough not to be dissolved entirely; the precipitate of ammonium metavanadate, which separated after a time, was collected on a filter, washed with a sufficient quantity of a saturated solution of ammonium chloride, dried and ignited. For the purpose of purification the remaining vanadium pentoxide, after it was moistened with a solution of ammonium nitrate and ignited, was dissolved in ammonia, and the solution evaporated until ammonia could scarcely be detected by the odor, then filtered, evaporated to dryness and ignited. Very exact analyses demand the collection of the small amount of ammonium metavanadate always remaining in the filtrate, and this is therefore evaporated to dryness and ignited. The residue is digested with some concentrated ammonia, the solution filtered, and precipitated with alcohol. The precipitate, dissolved in a little water, will give a solution, furnishing, when treated as above, with a lump of ammonium chloride, the small residue of ammonium metavanadate. The ignited mass (see above) may also—and this is a good method, after treatment with ammonia, heating to drive off the excess of ammonia, and filtration—be precipitated by lead acetate. The precipitate is then suspended in water, acidulated with nitric acid, and decomposed by means of hydrogen sulphide.[1] In this way a filtrate is formed which leaves on evaporation and ignition the whole balance of the vanadium pentoxide.

It was already mentioned before that the purpose of melting the ore for the second time with soda and saltpetre was to determine if any vanadium and chromium, and how much, were not extracted the first time. The result of these operations was that scarcely a trace of chromium and but little more than a trace of vanadium were found, so that, if the work is done in a careful way, a repetition of all the operations will surely be unnecessary.

A comparison of the two methods of treatment described shows that Treatment I is always to be preferred, if it is desired to estimate only the vanadium, because it furnishes at once a solution free from chromium, and the quantity of vanadium left in the ore is smaller, and, further, because a large porcelain crucible can generally be had more easily than a large platinum one.

It is, however, a fact known to every analytical chemist that platinum crucibles are always preferred to such of porcelain, provided there is no objection to use them. With this point in view, it seemed to me to be both interesting and important to ascertain if an addition of a smaller quantity of soda and saltpetre to the treated ore might suffice to decompose it perfectly. The ore or the residue left each time after the ignition and extraction with water on the filter was therefore subjected to these operations three times: the first time it was made strongly alkaline by means of soda and then mixed with the third part of its weight of saltpetre; the second time the residue on the filter was mixed with the third part of each of soda and saltpetre, and the third time double the quantity of an equal weight of each one was mixed with the residue. The result of the melting processes was that the solution obtained the first time was yellow; that of the second time yellowish, and that of the third time hardly yellowish; and while the amount of vanadium and chromium was the largest in the first solution, there was still an appreciable quantity of both in the second; but a little, however, of both in the third. On comparing this result with that above obtained, when the melting was done once only with a considerable quantity of soda and saltpetre, it seems to me clear that, in order to obtain a good result, it is not only advisable, but necessary, to add to the prepared ore about three times its weight of each of these substances.

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[1] A precipitate of lead chromate and lead vanadate was suspended in water, acidulated with nitric acid, and treated with sulphuretted hydrogen gas, which decomposed it easily and perfectly. A precipitate, however, of the above lead compounds and of lead sulphate (the last one in considerable excess) did not give an equally good result, although the gas was passed until a strong smell of it remained after standing. It was observed that the smell disappeared again entirely after several hours, although the vessel was well closed, thus showing that a complete decomposition had not taken place. As the same result was obtained after repeated treatment, the precipitate was separated by a filter from the liquid, and both subjected to several tests, which proved that the precipitate contained lead sulphate, lead vanadate and lead chromate, besides lead sulphide, while in the filtrate sulphuric, vanadic and chromic acids were found. The above method of decomposing a precipitate of lead vanadate and lead chromate is therefore without doubt a good one only if no lead sulphate, or but a little of it, is present; if, however, a large quantity of it is present, it would be a troublesome and tedious operation to effect the necessary thorough decomposition of the precipitate in this manner. In such a case treatment with chlorhydric acid and alcohol will answer the purpose quickly and satisfactorily.

WILLIAM RIPLEY NICHOLS.

The death of Prof. William Ripley Nichols removes from us not only one of the most eminent of American chemists, but also one of the most influential of American educators. Prof. Nichols combined in a rare degree the love of teaching and the love of science, and he introduced into his teaching the same scientific spirit which he showed in solving difficult problems pertaining to sanitary chemistry. He was one of the first to emphasise the importance of laboratory work even in the teaching of elementary chemistry. Yet he never made a fetich of this method of instruction, and always recognised the fact that the necessity for hard study was not removed by the use of this now fashionable mode of teaching. So he required his students to obtain not only skill in manipulation and accurate information concerning the properties of compounds, but also a thorough knowledge of the theoretical views that lie at the foundation of modern chemistry. Prof. Nichols believed that a thorough laboratory training in general chemistry was the best method for cultivating the habit of accurate observation and for teaching the fundamental rules for scientific investigation to all students, whether they were in later years to pursue the study of chemistry or any other branch of science.

William Ripley Nichols graduated from the Roxbury Latin School at the age of sixteen. He then spent two years in travel and study in Europe, and returned and entered Harvard University. Although a proficient and interested student of the classics, yet in a few months he became convinced that a purely scientific training would best fit him for the duties of manhood, and he withdrew from the University and connected himself as a student with the Massachusetts Institute of Technology, then in its infancy, and graduated from this school with the class of 1869. His proficiency in his favorite science caused him to be chosen immediately instructor in chemistry in the Institute; in 1870 he was chosen assistant professor, and in 1872 he was called to fill the chair of General Chemistry in the Institute of Technology, and he retained this position until his death.

His early researches were in the field of inorganic chemistry, but in 1870 he turned his attention to sanitary chemistry, and to what afterwards became his specialty—water supply and questions related to it. He was employed by the Massachusetts State Board of Health to examine into the sanitary condition of the prominent rivers of the State, and often consulted by this Board upon matters relating to the public health. His aid was invoked by the Water Boards of many cities, and his opinion on subjects relating to water supply had great weight not only in America, but also throughout Europe. He received a medal and diploma from the London Health Exhibition in recognition of his eminence as an authority and of aid rendered. His publications of considerable length, relating to sanitary chemistry, number forty-four. The most important among them is his well-known work, "Water Supply, Chemical and Sanitary," published in 1883.

But Prof. Nichols did not confine his literary activity to the field of sanitary chemistry. In conjunction with Prof. John Trowbridge and Dr. Samuel Kneeland he prepared the "Annals of Scientific Discovery" for 1869 and for 1870. He abridged and revised Eliot and Storer's "Manual of Inorganic Chemistry," and thus he produced the well-known Eliot and Storer's "Elementary Manual of Chemistry." He also revised the "Qualitative Analysis" by the same authors, and prepared, in connection with the writer, a book entitled "Laboratory Experiments."

Prof. Nichols brought to his work a strong frame, remarkable energy and patient application. His personal devotion to the interests of the Massachusetts Institute of Technology impressed all who knew him. No labor was too hard, no effort too great, if his loved Institute was to receive benefit from it. In 1881, in consequence, doubtless, of overwork, the disease which finally ended his life attacked him, and his last five years were years of continual pain and weakness. Twice he sought relief by aid of the surgeon's knife, but the second operation resulted fatally, and he died at Hamburg, Germany, on July 14, 1886, aged 39 years. His domestic life had been singularly happy, and to the devotion and care of his wife was due, in no small degree, the courage with which he fought deadly disease during these long years and the determination which enabled him while an invalid to continue his work with unabated zeal. His career had been a busy and useful one, and his upright character and his love of science will continue to live in the minds and aims of the many students who came under his influence.

L. M. NORTON.

NOTES.

Action of an Electric Current upon Anhydrous Hydrofluoric Acid.

In a paper[1] presented to the French Academy of Sciences during the month of July, H. Masson describes the results he obtained by subjecting anhydrous hydrofluoric acid to electrolysis. The hydrofluoric acid made by heating carefully dried potassium hydrogen fluoride (KF.HF) is placed in a platinum U tube, cooled down to —50° C. and then subjected to the action of an electric current from twenty Bunsen elements. The platinum U tube is provided with small platinum tubes at the upper ends, for the escape of the gases formed, and is closed with stoppers made of fluor spar, through which the platinum electrodes pass.

From the negative pole hydrogen is evolved, while from the positive pole a colorless gas escapes, in which crystallised silicon and boron burn, forming fluorides. Powdered arsenic and antimony, as well as sulphur and iodine, take fire when brought into contact with this gas, the last losing its color. In contact with water the gas is decomposed, yielding ozone and hydrofluoric acid. The metals are also attacked by it; powdered iron and manganese when heated burn in it brilliantly. Organic substances are violently attacked. Cork is at once carbonised and takes fire, while alcohol, ether, benzene, turpentine oil and petroleum also burn in contact with the gas. When the hydrogen from the negative pole comes in contact with the gas evolved from the positive, they combine with a violent explosion.

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[1] Compt. Rend. **103**, 202-205. Preliminary Note, *ibid.* **102**, 1543.

As a mixture of ozone and hydrofluoric acid does not show any of these reactions, and as the hydrofluoric acid used was shown to be absolutely free from chlorine, the author concludes that the gas evolved from the positive pole in the electrolysis of hydrofluoric acid is either fluorine or hydrogen perfluoride. In a later paper[1] on the same subject, he shows that this active gas is also obtained by the electrolysis of the fused potassium hydrogen fluoride (KF.HF), and that it undoubtedly is fluorine, and not hydrogen perfluoride. This is shown by the fact that it yields no hydrogen when passed over powdered iron heated to redness, and by the fact that the increase in weight which the iron shows in this experiment (due to the formation of iron fluoride) corresponds very nearly exactly to the quantity of hydrogen evolved from the negative pole, which was collected and measured.

W. R. O.

U. S. DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., *December* 9, 1886.

PROF. IRA REMSEN,
Editor American Chemical Journal.

Dear Sir :—In my recent address before Sec. C, A. A. A. S., at Buffalo, I gave a brief review of the present knowledge of nitrification and denitrification in their relations to plant-growth. In this summary I omitted to mention the paper[2] of Dr. Alfred Springer on denitrifying ferments. I feel quite sure that to him equally with Gayon and Dupetit belongs the honor of having discovered this ferment.

Hoping thus to do him tardy justice,

I am faithfully,

H. W. WILEY.

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[1] Compt. Rend. **103**, 256-258.

[2] This Journal **4**, No. 6. Proceedings Ohio Mechanics' Institute **2**, No. 1.